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Environmental Impacts of Discharge Water from Exhaust Gas Cleaning Systems on Ships

Final report of the project ImpEx

German Environment Agency

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Environmental Impacts of Discharge Water from Exhaust Gas Cleaning Systems on Ships

Final report of the project ImpEx

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Abstract: Environmental Impacts of Discharge Water from Exhaust Gas Cleaning Systems on Ships – Final report of the project ImpEx

Following the implementation of international regulations to reduce sulphur oxide emissions in maritime shipping, scrubbers are used on about 25 % of the world merchant fleet (measured by deadweight tonnage).

In the present study, a sampling and measurement campaign was conducted on board four ships with focus on the chemical characterisation and the determination of ecotoxicological effects of scrubber discharge water. Heavy metals such as vanadium, nickel, copper, iron and zinc as well as organic pollutants, including polycyclic aromatic hydrocarbons (even beyond the ones included in the US EPA priority list) and oil residues, were found in elevated concentrations. The whole effluent toxicity of the scrubber discharge waters ranged from practically non-toxic to considerably toxic for the open loop to extremely toxic for the closed loop operation mode samples. Further, almost all samples demonstrated mutagenic and the closed loop samples, dioxin-like effects. Thus, the release of scrubber discharge water from both operation modes into the sea is of high concern. This effluent is acidic and contains persistent, bioaccumulative and toxic pollutants that may cause short- and long-term detrimental effects in the marine environment.

In this regard, the current discharge criteria and regulatory measures were found to be insufficient and other protective measures for the marine environment such as local or regional discharge bans are proposed.

Kurzbeschreibung: Umweltauswirkungen von Scrubber-Abwasser aus Abgasnachbehandlungsanlagen auf Schiffen – Abschlussbericht vom Projekt ImpEx

Mit der Umsetzung von internationalen Vorschriften zur Reduzierung von Schwefeloxidemissionen in der Seeschifffahrt werden Scrubber auf etwa 25 % der weltweiten Handelsflotte (bezogen auf die Tragfähigkeit) eingesetzt.

In der vorliegenden Studie wurde eine Probenahme- und Messkampagne an Bord von insgesamt vier Schiffen durchgeführt, wobei der Schwerpunkt auf der chemischen Charakterisierung und der Bestimmung ökotoxikologischer Effekte des Scrubber-Abwassers lag. Schwermetalle, wie Vanadium, Nickel, Kupfer, Eisen und Zink, sowie organische Schadstoffe, einschließlich polyzyklischer aromatischer Kohlenwasserstoffe (sogar die über die in der Prioritätsliste der US EPA aufgeführten Stoffe hinausgehen) und Ölrückstände, wurden in erhöhten Konzentrationen gefunden. Die Gesamttoxizität der Scrubber-Abwässer reichte von praktisch ungiftig bis beträchtlich giftig bei den Open-Loop- und war extrem toxisch bei den Closed-Loop-Proben. Außerdem wurden bei fast allen Proben eine mutagene und bei den CL-Proben dioxinähnliche Wirkungen nachgewiesen. Aus diesen Gründen ist die Einleitung von Scrubber-Abwasser ins Meer aus beiden Betriebsmodi äußerst bedenklich. Dieses Abwasser ist säurehaltig und enthält persistente, bioakkumulierende und toxische Schadstoffe, die kurz- und langfristig schädliche Auswirkungen auf die Meeresumwelt haben können.

In dieser Hinsicht werden die derzeitigen Einleitkriterien und Regulierungsmaßnahmen als unzureichend beurteilt. In diesem Bericht werden andere Schutzmaßnahmen für die Meeresumwelt wie lokale oder regionale Einleitverbote vorgeschlagen.

Table of content

List of figures

List of tables

List of abbreviations

AHR	Aryl hydrocarbon receptor
BfG	*Bundesanstalt für Gewässerkunde* (German Federal Institute of Hydrology)
BSH	*Bundesamt für Seeschifffahrt und Hydrographie* (German Federal Maritime and Hydrographic Agency)
BTEX	Benzene, toluene, ethylbenzene and xylene
BUKEA	*Behörde für Umwelt, Klima, Energie und Agrarwirtschaft* (Ministry of Environment, Climate, Energy and Agriculture)
CL	Closed loop
CSC	Clean Shipping Coalition
ECA(s)	Emission Control Area(s)
EGCS	Exhaust gas cleaning system(s)
FNU	Formazin nephlometric units
FOEI	Friends of the Earth International
G	Acceleration value of the centrifuge expressed as gravitational force
GES	Good Environmental Status
GESAMP	Group of Experts on the Scientific Aspects of Marine Environmental Protection
GHG	Greenhouse gases
GT	Gross tonnage
hAHR	Human aryl hydrocarbon receptor
HELCOM	Baltic Marine Environment Protection Commission
HEREON	Helmholtz-Zentrum hereon GmbH
HFO	Heavy fuel oil
HOI	Hydrocarbon oil index
HU	Hamburg Institute for Hygiene and Environment
ICES	International Council for the Exploration of the Sea
IMO	International Maritime Organization
LID	Lowest ineffective dilution
LOD	Limit of detection
LOQ	Limit of quantification
LSFO	Low-sulphur fuel oil
MARPOL	International Convention for the Prevention of Pollution of Ships
MDO	Marine diesel oil
MEPC	IMO Marine Environment Protection Committee
MGO	Marine gas oil
MOSAB	Project Modelling discharge water and contaminant dispersion from scrubber in shipping to the marine environment
MSFD	Marine Strategy Framework Directive
NF-eq	β–Naphtoflavone equivalence concentration

NOEC	No-observed effect concentration
NOx	Nitrogen oxides
NTU	Nephelometric turbidity units
OL	Open loop
OSPAR	The Convention for the Protection of the Marine Environment of the North-East Atlantic
PAH	Polycyclic aromatic hydrocarbon(s)
PAH_{phe}	PAH as phenanthrene equivalent
PAK	*Polyzyklische aromatische Kohlenwasserstoffe*
PCB	Polychlorinated biphenyls
pH	Defined as decimal logarithm of the reciprocal of the hydrogen ion activity
PPR	IMO Sub-Committee on Pollution Prevention and Response
PSSA	Particularly Sensitive Sea Areas
PSU	Practical salinity unit
pT	*Potentia toxicologiae*
SOx	Sulphur oxides
SPE	Solid-phase extraction
TEF	Toxic equivalency factor
TEQ	Toxic equivalent
UBA	*Umweltbundesamt* (German Environment Agency)
UNCLOS	The United Nations Convention on the Law of the Sea
WET	Whole effluent toxicity
WWF	World Wide Fund for Nature
WWU	*Westfälische Wilhelms-Universität Münster* (University of Muenster)
YDS	Yeast dioxin screening

Summary

The use of exhaust gas cleaning systems (EGCS), commonly known as scrubbers, on seagoing ships has become widespread since the introduction of international regulations to reduce sulphur oxide (SOx) emissions in the maritime industry. About 25 % of the global merchant fleet (by dead-weight tonnage) is equipped with a scrubber system. The use of scrubbers is expected to continue in the long term, if regulations remain unchanged. Open loop (OL) systems (86.1 %) dominate the scrubber market, followed by hybrid systems (13.2 %), which can be operated in OL and closed loop (CL) mode. There are environmental concerns regarding the release of scrubber discharge water as not only SOx but also other pollutants from the exhaust gas such as heavy metals, oil residues and polycyclic aromatic hydrocarbons (PAH) end up in the water.

This report presents the results of the ImpEx project (2020-2023), which was carried out on behalf of the German Environment Agency (UBA) by a consortium of German federal agencies, state authorities and institutions. The project focused on the analyses of scrubber discharge water and the evaluation of the current regulation. The main aim was to contribute to a factual discussion on the concerns arising from scrubber discharge water in the marine environment. In this regard, an analysis of status quo based on a literature review was published in 2021 (Marin-Enriquez et al., 2021) within the framework of the project. A sampling and measurement campaign on board four ships equipped with scrubber hybrid systems was conducted with focus on the chemical characterisation and ecotoxicological effects of scrubber water samples, but also included the evaluation of the discharge water online monitoring and the characterisation of fuel and lube oil. The sampling and analyses followed the procedures provided in the sampling and analysis protocol (SAP) developed within the project (see Appendix C – Supplement A). The full results related to the chemical characterisation (i.e. chemical composition, emission factors, water treatment efficiency and water online monitoring) can be found in Supplement B[1].

The scrubber systems were sampled one time each under normal operating conditions in both operation modes (OL and CL). The specific flowrates of discharge water ranged from 0.20 to 3.5 m^3/MWh in CL and from 54 to 93 m^3/MWh in OL (without consideration of dilution water).

Chemical characterisation and emission factors of scrubber discharge water

The chemical characterisation of scrubber water samples included the determination of general parameters, nitrogen compounds, metals, rare-earth elements, organic compounds and non-target screening. Emission factors were calculated based on the specific water flowrates and expressed as mass of pollutant per energy output.

The discharge water temperature was 4 to 18 °C above inlet temperatures. The elevated temperature of the discharge water is considered in general not to be of environmental concern due to the expected high dilution in receiving waters, but impacts on aquatic ecosystems cannot be excluded for smaller enclosed water bodies, where temporary water temperature rise could occur. Three ships exceeded considerably the discharge criteria for turbidity (Δ25 FNU) in CL discharge.

The pH in the OL (3.0 – 4.9) and CL discharge water (5.6 – 7.1) was in the acidic range (≤ 6.5) except for one sample; while the alkalinity was depleted in the OL operation and ranged from 2.8 to 8.0 mmol/l in CL discharge water. As modelled in other studies, OL discharge water can have

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[1] Supplement B can be downloaded from the website: https://www.bsh.de/DE/THEMEN/Forschung_und_Entwicklung/Abgeschlossene-Projekte/_Anlagen/Downloads/sicherheit-und-umweltschutz/ImpEx_final_report_supplement_B.html.

acidification effects in harbors and their vicinities as well as in coastal areas with high shipping activity.

In most of the OL samples, the concentration of nitrogen compounds (i.e. total nitrogen, NO_3^-, NO_2^- and NH_4^+) was below the limit of quantification. In CL operation the enrichment of nitrogen compounds was evident with 35 to 66 g/MWh of total nitrogen. The capacity of the scrubber system for removal of nitrogen oxides (NOx) from the exhaust gas was estimated to be 2.1 % maximum. Considering these findings and the already in force NOx regulations, it was concluded that nitrates should not be in general a matter of concern in scrubber discharges. This conclusion might be taken cautiously for the discharges from CL, where the total nitrogen reached up to 220 mg/l and discharges usually take place at specific points like in the proximity of areas with a discharge ban.

Heavy metals such as vanadium, nickel, copper, iron and zinc were found in elevated concentrations, with higher concentrations in CL than in OL. For instance, the concentrations of nickel and vanadium were on average about 40 times higher in CL (V: 1500 – 19700 µg/l; Ni: 410 – 3470 µg/l) than in OL (V: 140 – 308 µg/l; Ni: 40 – 73 µg/l). Fuel and lube oil as well as corrosion of ship's and scrubber system's materials, including the sampling points themselves, are pointed out as relevant sources for the enrichment of heavy metals in scrubber discharge water. Enrichment of arsenic, chromium and lead was demonstrated in CL discharge samples; on that basis and despite the low concentrations in OL discharge (mostly below the limit of quantification), there might be a potential enrichment of these metals in OL operation. The presence of cadmium and mercury in discharge water might be exclusively related to the environmental concentrations as their potential enrichment was determined to be extremely low. Metals were determined in untreated and filtered samples to calculate the dissolved fractions. The dissolved fraction of nickel and vanadium in OL discharge water was close to 40 % and in CL above 90 %.

To our knowledge, the analysis of rare-earth elements, such as cerium, lanthanum and yttrium, in scrubber discharge water is a novelty of this study. The evaluation of the results showed that there is an enrichment in the discharge water with estimated emission factors <10 mg/MWh.

Hydrocarbon oil index (HOI) was determined as indicator of the oil content in the water samples. The oil content in OL discharge was in the range of 0.1 – 1.3 mg/l; three out of the four samples exceeded 1 mg/l slightly. It should be noted that there is no discharge limit for oil content in scrubber discharge water. However, 1 mg/l served as reference to define the discharge limit of PAH as surrogate parameter. CL discharge showed oil concentrations between <0.1 and 8.1 mg/l and on average 4.6 times higher than in OL.

Besides the 16 priority PAH (16 EPA PAH), an extended list of PAH covering about 70 compounds (incl. alkylated PAH) was analyzed, since there are PAH of much higher toxicity than the 16 EPA PAH. The sum of the 16 EPA PAH in OL discharge was in the range of 1.7 – 55.6 µg/l, while in CL discharge it ranged between 6.9 and 150 µg/l. The 16 EPA PAH discharge concentrations of two ships were much higher than the average values reported in the literature (Hermansson et al., 2021). It was assumed that a poor combustion efficiency is the main factor explaining these high concentrations as no issues were found in the sampling and analysis procedures. In OL discharge 16 EPA PAH dominated in dissolved form, while 16 EPA PAH in particulate form dominated in CL discharge. The most abundant 16 EPA PAH species were phenanthrene, naphthalene and fluorene. The total concentration of the extended list of PAH was on average four-fold higher than the sum of 16 EPA PAH in OL and CL discharge water. There was a mixed source of the alkylated PAH, i.e. a combination of rather petrogenic naphthalenes and rather pyrogenic higher molecular PAH. The alkylated PAH dominated the total PAH concentrations and, as expected in the dissolved fractions, were mainly low-molecular weight PAH.

The sum of benzene, toluene, ethylbenzene and xylene was in the range of 0.3 – 2.8 µg/l in OL and 1.7 – 46.1 µg/l in CL discharge, with benzene being the most abundant. Highly volatile halogenated hydrocarbons were not found in any sample, except for dichloromethane (0.7 µg/l) in one CL discharge sample. Polychlorobiphenyls and dioxins concentrations were below the limit of quantification in all water samples.

The emission factors for vanadium (9.3 – 17.8 g/MWh in OL; 2.8 – 10.0 g/MWh in CL) and for nickel (2.8 – 4.2 g/MWh in OL; 0.7 – 2.3 g/MWh in CL) were on average about three times higher in OL than in CL operation. The emission factors for oil residues (7.5 – 121 g/MWh in OL; 0.04 – 24 g/MWh in CL) and for 16 EPA PAH (116 – 2987 mg/MWh in OL; 2.3 – 519 mg/MWh in CL) were on average 64 and 150 times higher, respectively, in OL operation than in CL operation.

Water treatment removal efficiency

The notably lower emission factors in CL can be partly explained by the water treatment removal efficiencies. Nickel (34 %) and vanadium (43 %) showed on average lower removal rates than oil content (80 %) and 16 EPA PAH (66 %) in the bleed-off treatment unit in CL operation. Thus, hydrocarbons were more easily removed than metals. This can be explained by the higher abundance of the hydrocarbons in particulate form and the higher solubility of metals. In CL operation, the water treatment equipment on board the sampled vessels consisted of centrifugal separation (with or without addition of flocculants) or dissolved air flotation (with addition of flocculants). Both ships with flocculant addition showed notably higher removal rates. Three out of the four sampled ships included a water treatment step (hydrocyclone) in the OL operation. One of them was sampled upstream and downstream; the results showed very low and even negative removal rates. Therefore, the usefulness of this water treatment step in OL operation is questioned.

Online monitoring evaluation

The ships' online monitoring data were evaluated for consistency and plausibility and compared to own measurements of pH, turbidity and PAH as phenanthrene equivalent (PAH_{phe}). The results of the evaluation substantiate the issues reported by other studies and question the reliability of onboard online monitoring for scrubber water discharges. The correct installation of the sensors following the manufacturer's specifications, periodic cleaning, calibration and maintenance are essential for reliable functioning of the measuring equipment and accurate monitoring.

The usefulness of PAH_{phe} monitoring (as surrogate parameter for oil content) was assessed by comparing the own measurements of PAH_{phe} with the laboratory results of phenanthrene, sum of 16 EPA PAH and oil content. It was observed that phenanthrene, 16 EPA PAH and oil content are strongly related to PAH_{phe} in OL discharge. In fact, the PAH_{phe} values were practically equivalent to the sum of 16 EPA PAH with an offset close to 7. Oil content seemed to be about 30 times higher than PAH_{phe} so that oil content of 1 mg/l corresponds to a PAH_{phe} concentration of around 40 µg/l. In CL discharge, there is a weaker relation of phenanthrene and 16 EPA PAH with PAH_{phe}; while no relation was obtained with oil content. As conclusion, PAH_{phe} is a suitable surrogate parameter for oil content in OL discharge water but not in CL discharge.

Further, the technical feasibility for onboard online monitoring of nitrates was demonstrated. However, no further efforts were undertaken on this topic as nitrates might not be relevant in conventional scrubber systems and the current regulation does not require the onboard monitoring of these compounds.

Ecotoxicity of scrubber discharge water

For the ecotoxicological assessment of the scrubber water samples, a combination of whole effluent toxicity (WET) tests on three marine species (luminescent bacteria, marine algae and marine copepods) representing three trophic levels and two specific tests for mutagenic and dioxin-like effects were selected. Additionally, acute fish-egg toxicity testing with zebrafish was included to complement the test battery by a vertebrate species. The WET tests were conducted with the native samples; while for the specific-toxicity and fish-egg tests the samples were subjected to solid-phase extraction prior to testing.

All WET tests were performed in compliance with international ISO standards and met all validity criteria specified in the corresponding standard, including pH adjustment for acidic samples. WET testing allowed for the assessment of the combined toxic effects of all contaminants contained in the water samples to a range of aquatic organisms. The toxicity of each water sample was determined by the lowest ineffective dilution in each test and then classified from non-toxic to extremely toxic according to the most sensitive test species. Generally, the effects of the CL discharge samples (all extremely toxic) were much higher than of the OL discharge samples (between practically non-toxic and considerably toxic). The highest sensitivity to most of the scrubber water and discharge samples was shown by the copepods, followed by the marine algae, which proved to be more sensitive in one-third of the samples. There was no difference in the overall toxicity between the sampling points in CL (except for one ship), indicating that bleed-off treatment was ineffective in lowering the toxic load.

The effects in the yeast dioxin screening (dioxin-like effects) were higher for the CL than the OL discharge water samples. This observation showed some coherence with the oil content and 16 EPA PAH concentrations of the CL samples.

Ames tests were conducted with different strains (TA98, TA100, YG1041 and YG1042), with and without metabolic activation, to evaluate mutagenic effects. All discharge samples showed mutagenic potency in at least one of the bacterial strains although overall the OL discharge samples were less mutagenic than the CL discharge samples. However, strains YG1041 and YG1042 differ in their sensitivity compared to strains TA98 and TA100, since they additionally exhibit specificity toward promutagenic aromatic amines and nitroaromatic compounds. Thus, strains YG1041 and YG1042 showed mutagenic activity of OL discharge samples whereas strains TA98 and TA100 did not. Most CL samples, on the other hand, showed the highest possible number of revertant colonies (i.e. 100 % effect) in at least one of the four strains. Yet, there was distinct variation between the sampled ships.

Fish-egg tests did not provide consistent results that could have been used for an overall evaluation. Therefore, the test results are not shown in this report.

Fuel and lube oil composition

Fuel and, to a lesser extent, lube oil contribute to the presence of pollutants in scrubber discharge water. The concentration of heavy metals and 16 EPA PAH in fuel and lube oils used on board was determined. In addition, sulphur content was determined in the fuel oil samples. The ships operated with heavy fuel oil (HFO) with sulphur content between 2.1 % and 3.2 %. In general, the metal concentrations found in the fuel oil samples were close to the average values reported in the literature; only iron, nickel, vanadium and zinc showed values above the limit of quantification. The mass fraction of 16 EPA PAH in fuel oil was between 0.3 and 0.7 %, with the distribution of the 16 EPA PAH varying strongly between the samples, as expected. However, naphthalene and phenanthrene showed the highest average concentrations.

The potential emission factors of metals from fuel oil combustion were calculated and compared with the emission factors from OL discharge water. On average, the scrubbing process captured 36 % of nickel and 41 % of vanadium, which end up in the discharge water. For iron and zinc, no clear relation was found between water discharge and fuel oil composition, which indicated additional pollution sources besides fuel oil.

The lube oil samples generally had low metal concentrations, with the exception of zinc (350 – 500 mg/kg), along with nickel and vanadium, which were found in the fuel oil at high concentrations. These may have accumulated after continuous use of the lube oil in the combustion system. The concentration of 16 EPA PAH in lube oil samples were mostly below the limit of quantification.

Evaluation of current scrubber discharge regulation and potential regulatory measures

The current regulation from the International Maritime Organization (IMO) related to scrubber discharge water was found to be insufficient to provide the necessary protection for the marine environment. The ‘2021 EGCS Guidelines’ (resolution MEPC.340(77)) are only focused on the prevention of acute effects and do not ensure sufficient protection for the marine environment in the long term (chronic effects) as well as do not represent any practical restriction on OL discharges. A review of the discharge criteria set out in these guidelines was not considered to be very effective as they would only apply to new installations.

The recently adopted “Guidelines for risk and impact assessments of the discharge water from EGCS” (circular MEPC.1/Circ.899) advise that an environmental risk assessment should be carried out according to a unified approach when local or regional restrictions are considered. This measure has been assessed as not being highly effective. Conducting risk and impact assessments is time-consuming and costly, which could delay the designation of restricted areas. Further, this measure does not ensure a global protection as it depends on the initiative of single States to call for restrictions in their territorial waters only. Therefore, additional measures are considered necessary and there is a chance to bring new measures to IMO for discussion. A globally harmonized requirement for a discharge ban in coastal waters and/or territorial sea is considered to be an appropriate measure with a high degree of protection and with possibilities for acceptance in the IMO committees as well as near-term implementation. Since the shipping industry is familiar with restrictions inside the 12-nautical mile zone, the application of this measure seems straightforward. A disadvantage of this measure could arise if the CL is operated in ‘zero discharge’ mode. In that case, the stored water in the holding tank would probably be discharged near the borders of the restricted areas, which could increase the risk of development of hotspots. Therefore, as an accompanying measure, moderate discharge flowrates for stored water could be advised.

In the assessment process of potential protective measures, it is important to take into consideration the existing environmental regulatory framework, the estimated timescale for implementation and whether the measures also apply to existing installations.

Conclusions

The results presented in the report, as well as the results of other studies that have been reviewed indicate that there are potential detrimental effects for marine ecosystems from scrubber discharge water. Further studies and models can help to better understand effects in the marine environment, however, it is recommended to protect sensitive or highly polluted areas such as the Baltic Sea from discharges as soon as possible.

The discussion about protective measures with regard to scrubber discharges needs to be urgently addressed in the relevant committees at international, regional and national level.

Finally, the use of scrubbers is questionable even as a transitional technology. Specially, in view of climate protection, the use of alternative fuels should be pushed forward, which would phase out the use of scrubbers at all.

Zusammenfassung

Der Einsatz von Abgasnachbehandlungsanlagen (EGCS), gemeinhin als Scrubber bezeichnet, auf Seeschiffen ist seit der Einführung internationaler Vorschriften zur Reduzierung von Schwefeloxidemissionen (SOx) in der Seeschifffahrt weit verbreitet. Etwa 25 % der Welthandelsflotte (nach Tragfähigkeit) sind mit einem Scrubbersystem ausgestattet. Momentan ist davon auszugehen, dass der Einsatz von Scrubbern langfristig anhalten wird, wenn die Rechtsvorschriften nicht geändert werden. Der Markt für Scrubber wird von Systemen mit offenem Kreislauf (OL) beherrscht (86,1 %), gefolgt von Hybridsystemen (13,2 %), die sowohl im OL- als auch im geschlossenen Kreislauf (CL) betrieben werden können. Es bestehen ökologische Bedenken hinsichtlich der Einleitung von Scrubber-Abwasser, da nicht nur SOx, sondern auch andere Schadstoffe aus dem Abgas wie Schwermetalle, Ölrückstände und polyzyklische aromatische Kohlenwasserstoffe (PAK) in die Meeresumwelt gelangen.

Der vorliegende Bericht stellt die Ergebnisse des Projektes ImpEx (2020-2023) dar, das im Auftrag des Umweltbundesamtes (UBA) von einem Konsortium aus deutschen Bundesbehörden, Landesbehörden und Institutionen durchgeführt wurde. Der Schwerpunkt des Projekts lag auf der Analyse von Scrubber-Abwasser und der Bewertung der aktuellen Rechtsvorschriften. Hauptziel war es, zur Versachlichung der Diskussion über mögliche Bedenken beizutragen, die sich aus der Einleitung von Scrubber-Abwasser in die Meeresumwelt ergeben. In diesem Zusammenhang wurde im Rahmen des Projektes eine Analyse des Status quo anhand einer Literaturrecherche veröffentlicht (Marin-Enriquez et al., 2021). Eine Probenahme- und Messkampagne an Bord von vier Schiffen, die mit Scrubber-Hybridsystemen ausgestattet sind, wurde mit besonderem Augenmerk auf die chemische Charakterisierung und die ökotoxikologischen Auswirkungen des Scrubber-Abwassers durchgeführt, umfasste aber auch die Auswertung der Online-Überwachung des Abwassers und die Charakterisierung von Kraftstoff- und Schmierölproben. Die Probenahmen und Analysen erfolgten nach den Verfahren des im Rahmen des Projektes entwickelten Probenahme- und Analyseprotokolls (SAP, siehe Appendix C – Supplement A). Die vollständigen Ergebnisse aus der chemischen Charakterisierung (d. h. chemische Zusammensetzung, Emissionsfaktoren, Wirkungsgrad der Wasseraufbereitung und Online-Monitoring des Wassers) sind in ‚Supplement B‘[2] zu finden.

Die Scrubbersysteme wurden unter normalen Betriebsbedingungen in beiden Betriebsmodi (OL und CL) jeweils einmal beprobt. Die spezifischen Durchflussraten des Abwassers reichten von 0,20 bis 3,5 m^3/MWh in CL und von 54 bis 93 m^3/MWh in OL (ohne Berücksichtigung des Verdünnungswassers).

Chemische Charakterisierung und Emissionsfaktoren des Scrubber-Abwassers

Die chemische Charakterisierung der Scrubberwasserproben umfasste die Bestimmung von allgemeinen Parametern, Stickstoffverbindungen, Metallen, organischen Verbindungen und Non-Target-Screening. Die Temperatur des Abwassers lag 4 bis 18 °C über der Temperatur des Zulaufs. Die erhöhte Temperatur des Abwassers wird aufgrund der zu erwartenden starken Verdünnung in den aufnehmenden Gewässern im Allgemeinen als unbedenklich für die Umwelt angesehen. Doch können Auswirkungen auf aquatische Ökosysteme bei kleineren geschlossenen Gewässern, in denen es zu einem vorübergehenden Anstieg der Wassertemperatur kommen kann, nicht ausgeschlossen werden. Drei Schiffe überschritten die Einleitkriterien für die Trübung (Δ25 FNU) im CL-Abwasser erheblich.

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[2] Das ‚Supplement B’ kann auf folgender Website heruntergeladen werden: https://www.bsh.de/DE/THEMEN/Forschung_und_Entwicklung/Abgeschlossene-Projekte/_Anlagen/Downloads/sicherheit-und-umweltschutz/ImpEx_final_report_supplement_B.html.

Der pH-Wert im Abwasser von OL (3,0 – 4,9) und CL (5,6 – 7,1) lag mit Ausnahme einer Probe im sauren Bereich (≤ 6,5), während die Alkalinität im OL-Betrieb abnahm und im CL-Abwasser zwischen 2,8 und 8,0 mmol/l lag. Wie in anderen Studien modelliert wurde, kann OL-Abwasser Versauerungseffekte in Häfen und deren Umgebung sowie in Küstengebieten mit hoher Schifffahrtsaktivität haben.

In den meisten OL-Proben lag die Konzentration von Stickstoffverbindungen (d. h. Gesamtstickstoff, NO_3^-, NO_2^- und NH_4^+) unter der Bestimmungsgrenze. Im CL-Betrieb war die Anreicherung von Stickstoffverbindungen mit 35 bis 66 g/MWh Gesamtstickstoff offensichtlich. Die Kapazität des Scrubbersystems zur Entfernung von Stickoxiden (NOx) aus dem Abgas wurde auf maximal 2,1 % geschätzt. In Anbetracht dieser Ergebnisse und der bereits geltenden NOx-Vorschriften kann geschlussfolgert werden, dass Nitrate in Scrubber-Abwasser im Allgemeinen kein Problem darstellen sollten. Diese Schlussfolgerung sollte jedoch für das Abwasser von CL mit Vorsicht betrachtet werden, da der Gesamtstickstoff bis zu 220 mg/l erreicht und die Einleitungen in der Regel an bestimmten Stellen erfolgen, z. B. in der Nähe von Gebieten mit einem Einleitverbot.

Schwermetalle wie Vanadium, Nickel, Kupfer, Eisen und Zink wurden in erhöhten Konzentrationen gefunden, wobei die Konzentrationen in CL höher waren als in OL. So waren beispielsweise die Konzentrationen von Nickel und Vanadium im Durchschnitt etwa 40-mal höher in CL (V: 1500 – 19700 µg/l; Ni: 410 – 3470 µg/l) als in OL (V: 140 – 308 µg/l; Ni: 40 – 73 µg/l). Als wesentliche Quellen für die Anreicherung von Schwermetallen im Scrubber-Abwasser werden Treibstoff und Schmieröl sowie die Korrosion von Schiffs- und Scrubbersystemmaterialien, einschließlich der Probenahmestellen selbst, genannt. Eine Anreicherung von Arsen, Chrom und Blei wurde in CL-Abwasserproben nachgewiesen. Auf dieser Grundlage und trotz der niedrigen Konzentrationen in den OL-Abwasserproben (meist unterhalb der Bestimmungsgrenze), wird es davon ausgegangen, dass Arsen, Chrom und Blei im OL-Betrieb ein Anreicherungspotenzial haben. Das Vorhandensein von Cadmium und Quecksilber in den Abwässern könnte ausschließlich auf die Umweltkonzentrationen zurückzuführen sein, da ihre potenzielle Anreicherung als äußerst gering eingestuft wurde. Die Metalle wurden in unbehandelten und gefilterten Proben bestimmt, um die gelösten Fraktionen zu berechnen. Der gelöste Anteil von Nickel und Vanadium in den Abwässern von OL liegt bei fast 40 % und in CL bei über 90 %.

Unseres Wissens ist die Analyse von Seltenen Erden wie Cer, Lanthan und Yttrium im Scrubber-Abwasser ein Novum in dieser Studie. Die Auswertung der Ergebnisse zeigte, dass es eine Anreicherung im Abwasser mit geschätzten Emissionsfaktoren <10 mg/MWh gibt.

Der Mineralölkohlenwasserstoff-Index wurde als Indikator für den Ölgehalt in den Wasserproben bestimmt. Der Ölgehalt der OL-Abwasserproben lag im Bereich von 0,1 – 1,3 mg/l; drei der vier Proben überschritten leicht 1 mg/l. Es ist zu beachten, dass es keinen Grenzwert für den Ölgehalt im Scrubber-Abwasser gibt, jedoch diente 1 mg/l als Referenz, um den Grenzwert für die Einleitung von PAK als Ersatzparameter zu definieren. Die CL-Abwässer wiesen Ölkonzentrationen zwischen <0,1 und 8,1 mg/l auf und waren im Durchschnitt 4,6-mal höher als in OL.

Neben den 16 prioritären PAK-Schadstoffen (16 EPA-PAK) wurde eine erweiterte Liste von PAK mit etwa 70 Verbindungen (einschließlich alkylierter PAK) analysiert, da es PAK gibt, deren Toxizität wesentlich höher ist als die der 16 EPA-PAK. Die Summe der 16 EPA-PAK im OL-Abwasser lag in dem Bereich zwischen 1,7 und 55,6 µg/l, während sie im CL-Abwasser zwischen 6,9 und 150 µg/l lag. Die Konzentrationen der 16 EPA-PAK in den Abwässern von zwei Schiffen waren viel höher als die in der Literatur angegebenen Durchschnittswerte. Es ist davon auszugehen, dass eine schlechte Verbrennungseffizienz der Hauptfaktor ist, der diese hohen Konzentrationen erklärt; es wurden keine Mängel bei den Probenahme- und Analyseverfahren festgestellt. Die 16 EPA-PAK in gelöster Form dominierten im OL-Abwasser, während 16 EPA-PAK in partikulärer Form im CL-Abwasser dominierten. Die am häufigsten vorkommenden 16 EPA-PAK waren Phenanthren, Naphthalin und Fluoren. Die Gesamtkonzentration der erweiterten PAK-Liste war im Durchschnitt vierfach höher als die Summe der 16 EPA-PAK im OL- und CL-Abwasser. Es gab eine gemischte Quelle für die alkylierten PAK, d. h. eine Kombination aus eher petrogenen Naphthalinen und eher pyrogenen höhermolekularen PAK. Die alkylierten PAK dominierten die Gesamt-PAK-Konzentrationen und, wie erwartet, waren in den gelösten Fraktionen hauptsächlich niedermolekulare PAK.

Die Summe von Benzol, Toluol, Ethylbenzol und Xylol lag im Bereich von 0,3 – 2,8 µg/l im OL- und 1,7 – 46,1 µg/l im CL-Abwasser, wobei Benzol die höchsten Konzentrationen aufwies. Leichtflüchtige halogenierte Kohlenwasserstoffe wurden in keiner Probe gefunden, mit Ausnahme von Dichlormethan (0,7 µg/l) in einer CL-Abwasserprobe. Die Konzentrationen von Polychlorierten Biphenylen und Dioxinen waren in allen Wasserproben unterhalb der Bestimmungsgrenze.

Die Emissionsfaktoren für Vanadium (9,3 – 17,8 g/MWh in OL; 2,8 – 10,0 g/MWh in CL) und für Nickel (2,8 – 4,2 g/MWh in OL; 0,7 – 2,3 g/MWh in CL) waren im OL-Betrieb durchschnittlich etwa 3-fach höher als im CL. Die Emissionsfaktoren für Ölrückstände (7,5 – 121 g/MWh in OL; 0,04 – 24 g/MWh in CL) und für 16 EPA-PAK (116 – 2987 mg/MWh in OL; 2,3 – 519 mg/MWh in CL) waren im OL-Betrieb im Durchschnitt 64- bzw. 150-mal höher als im CL-Betrieb.

Wirkungsgrad der Wasseraufbereitung

Die deutlich niedrigeren Emissionsfaktoren im CL-Betrieb lassen sich teilweise durch die Wirkungsgrade bei der Wasseraufbereitung erklären. Nickel (34 %) und Vanadium (43 %) wiesen durchschnittlich geringere Reinigungsraten auf als der Ölgehalt (80 %) und 16 EPA-PAK (66 %) in der Wasseraufbereitungsanlage im CL-Betrieb. Kohlenwasserstoffe wurden demnach leichter entfernt als Metalle. Dies lässt sich durch die größere Verteilung der Kohlenwasserstoffe in partikulärer Form erklären. Die Wasseraufbereitungsanlagen im CL-Betrieb auf den beprobten Schiffen bestanden aus Zentrifugalabscheidung (mit oder ohne Zusatz von Flockungsmitteln) oder Druckentspannungsflotation (mit Zusatz von Flockungsmitteln). Beide Schiffe mit Flockungsmittelzusatz wiesen deutlich höhere Abscheideraten auf. Drei der vier beprobten Schiffe enthielten eine Wasseraufbereitungsstufe (Hydrozyklon) im OL-Betrieb. Bei einem dieser Schiffe wurden Proben vor und nach Behandlung entnommen; die Ergebnisse zeigten sehr niedrige und sogar negative Abscheideraten. Daher wird die Sinnhaftigkeit der Wasseraufbereitungsstufe im OL-Betrieb in Frage gestellt.

Auswertung des Online-Monitorings

Die Online-Monitoring-Daten der Schiffe wurden auf Konsistenz und Plausibilität geprüft und mit eigenen Messungen von pH-Wert, Trübung und PAK als Phenanthren-Äquivalent (PAK_{phe}) verglichen. Die Auswertung bestätigte die in anderen Studien berichteten Probleme und stellte die Zuverlässigkeit des Online-Monitorings von Scrubber-Abwässern an Bord in Frage. Der korrekte Einbau der Sensoren gemäß den Herstellerangaben, die regelmäßige Reinigung, Kalibrierung und Wartung sind für das zuverlässige Funktionieren der Messgeräte und eine genaue Überwachung unerlässlich.

Die Sinnhaftigkeit des PAK_{phe}-Monitorings (als Ersatzparameter für den Ölgehalt) wurde durch den Vergleich der eigenen Messungen von PAK_{phe} mit den Laborergebnissen von Phenanthren, der Summe der 16 EPA-PAK und dem Ölgehalt bewertet. Es wurde festgestellt, dass Phenanthren, 16 EPA-PAK und der Ölgehalt in engem Zusammenhang mit dem PAK_{phe} in

OL-Abwässern stehen. Tatsächlich entsprachen die PAK_{phe}-Werte der Summe von 16 EPA-PAK mit einem Offset von etwa 7. Der Ölgehalt scheint das 30-fache des PAK_{phe} zu betragen, so dass ein Ölgehalt von 1 mg/l einer PAK_{phe}-Konzentration von etwa 40 µg/l entspricht. In CL-Abwasser gibt es einen schwächeren Zusammenhang zwischen Phenanthren und PAK_{phe} sowie zwischen 16 EPA-PAK und PAK_{phe}, während für den Ölgehalt keine Korrelation mit PAK_{phe} festgestellt wurde. Daraus lässt sich schließen, dass PAK_{phe} ein sehr guter Ersatzparameter für den Ölgehalt in OL-Abwässern ist, nicht aber in CL-Abwässern.

Außerdem wurde die technische Machbarkeit eines Online-Monitorings von Nitraten an Bord nachgewiesen. Das Thema Nitrat-Messung wurde im Rahmen des Projektes nicht weiter vertieft, da Nitrate im Abwasser konventioneller Scrubber-Systeme wenig relevant sind und die derzeitige Richtlinie die bordseitige Überwachung dieser Verbindungen nicht vorschreibt.

Ökotoxizität des Scrubber-Abwassers

Für die ökotoxikologische Bewertung der Scrubber-Wasserproben wurde eine Kombination aus Tests zur Gesamttoxizität des Abwassers (WET-Test) an drei marinen Arten (Leuchtbakterien, marine Algen und marine Kopepoden), die drei trophische Ebenen vertreten, und aus zwei spezifischen Tests für mutagene und dioxinähnliche Wirkungen ausgewählt. Um diese Testpalette durch eine aquatische Wirbeltierart zu ergänzen, wurde die akute Toxizität von Proben auf Zebrafischeier einbezogen. Die WET-Tests wurden mit den nativen Proben durchgeführt, während die Proben für die Tests zur spezifischen Toxizität und zu Fischeiern einer Festphasenextraktion unterzogen wurden.

Alle WET-Tests wurden in Übereinstimmung mit internationalen ISO-Normen durchgeführt und erfüllten alle in der entsprechenden Norm festgelegten Validitätskriterien, einschließlich der Anpassung des pH-Werts bei sauren Proben. Die WET-Tests ermöglichten die Bewertung der kombinierten toxischen Wirkung aller in den Wasserproben enthaltenen Schadstoffe auf eine Reihe von Wasserorganismen. Die Toxizität jeder Wasserprobe wurde durch die niedrigste unwirksame Verdünnung in jedem Test bestimmt und dann entsprechend der empfindlichsten Testspezies von nicht toxisch bis extrem toxisch eingestuft. Im Allgemeinen waren die Wirkungen der CL-Abwasserproben (alle extrem toxisch) viel höher als die der OL-Abwasserproben (zwischen praktisch toxisch und beträchtlich toxisch). Die höchste Empfindlichkeit gegenüber den meisten Waschwasser- und Abwasserproben zeigten die Kopepoden, gefolgt von den Algen, die sich bei einem Drittel der Proben als empfindlicher erwiesen. Es gab keinen Unterschied in der Gesamttoxizität zwischen den Probenahmepunkten in CL (außer bei einem Schiff), was darauf hindeutet, dass die Behandlung des Bleed-Offs die toxische Belastung nicht wirksam senkte.

Die Effekte im Hefe-Dioxin-Screening (dioxinähnliche Wirkung) waren bei den CL- höher als bei den OL-Abwasserproben. Diese Beobachtung zeigte eine gewisse Kohärenz mit dem Ölgehalt und den 16 EPA-PAK-Konzentrationen der CL-Proben.

Ames-Tests wurden mit verschiedenen Stämmen (TA98, TA100, YG1041 und YG1042) mit und ohne metabolische Aktivierung durchgeführt, um mutagene Wirkungen zu bewerten. Alle Abwasserproben zeigten eine mutagene Potenz in mindestens einem der Bakterienstämme, obwohl die OL-Abwasserproben insgesamt weniger mutagen waren als die CL-Abwasserproben. Die Stämme YG1041 und YG1042 unterscheiden sich jedoch in ihrer Sensitivität gegenüber den Stämmen TA98 und TA100, da sie zusätzlich eine Spezifität gegenüber promutagenen aromatischen Aminen und Nitroaromaten aufweisen. Somit zeigten die Stämme YG1041 und YG1042 mutagene Aktivität bei den OL-Abwasserproben, während die Stämme TA98 und TA100 dies nicht taten. Andererseits zeigten die meisten CL-Proben in mindestens einem der vier

Stämme die höchstmögliche Anzahl von Revertantenkolonien (d. h. 100 % Wirkung). Es gab jedoch deutliche Unterschiede zwischen den beprobten Schiffen.

Die Fischei-Tests lieferten keine konsistenten und validen Ergebnisse und wurden daher nicht in die ökotoxikologische Bewertung aufgenommen. Die Testergebnisse werden in diesem Bericht nicht dargestellt.

Zusammensetzung von Kraftstoff und Schmieröl

Der Kraftstoff und in geringerem Maße auch Schmieröl tragen zum Vorhandensein von Schadstoffen im Scrubber-Abwasser bei. Die Konzentration von Schwermetallen und 16 EPA-PAK in den an Bord verwendeten Kraftstoffen und Schmierölen wurde bestimmt. Darüber hinaus wurde der Schwefelgehalt in den Kraftstoffproben bestimmt. Die Schiffe wurden mit Schweröl mit einem Schwefelgehalt zwischen 2,1 % und 3,2 % betrieben. Im Allgemeinen lagen die in den Kraftstoffproben gefundenen Metallkonzentrationen in etwa bei den in der Literatur angegebenen Mittelwerten; Eisen, Nickel, Vanadium und Zink waren die Metalle mit Ergebnissen oberhalb der Bestimmungsgrenze. Der Massenanteil der 16 EPA-PAK in Kraftstoff lag zwischen 0,3 und 0,7 %, wobei die Verteilung der 16 EPA-PAK zwischen den Proben erwartungsgemäß stark variierte. Naphthalin und Phenanthren wiesen jedoch die höchsten Mittelwertkonzentrationen auf.

Die potentiellen Emissionsfaktoren von Metallen aus der Kraftstoffverbrennung wurden berechnet und mit den Emissionsfaktoren aus dem OL-Abwasser verglichen. Im Durchschnitt wurden bei der Auswaschung 36 % des Nickels und 41 % des Vanadiums aufgefangen, die in das Abwasser gelangten. Bei Eisen und Zink wurde kein eindeutiger Zusammenhang zwischen dem Abwasser und der Zusammensetzung des Kraftstoffs festgestellt, was auf zusätzliche Verschmutzungsquellen neben dem Kraftstoff hinweist.

Die Schmierölproben wiesen im Allgemeinen niedrige Metallkonzentrationen auf mit Ausnahme von Zink (350 – 500 mg/kg) sowie Nickel und Vanadium, die im Kraftstoff in hohen Konzentrationen gefunden worden sind. Diese könnten sich nach der kontinuierlichen Verwendung des Schmieröls im Verbrennungssystem angesammelt haben. Die Konzentrationen von 16 EPA-PAK in Schmierölproben waren meist unterhalb der Bestimmungsgrenze.

Bewertung der derzeitigen Vorschriften für Scrubber-Abwasser und mögliche regulatorische Maßnahmen

Die derzeitige Regelung der Internationalen Seeschifffahrtsorganisation (IMO) in Bezug auf Scrubber-Abwasser wurde als nicht ausreichend erachtet, um den erforderlichen Schutz der Meeresumwelt zu gewährleisten. Die "EGCS-Leitlinien 2021" (Entschließung MEPC.340(77)) sind nur auf die Verhinderung akuter Auswirkungen ausgerichtet, bieten auf lange Sicht keinen ausreichenden Schutz für die Meeresumwelt (Akkumulationseffekte) und beinhalten keine praktischen Einschränkungen für das Einleiten von OL-Abwasser. Eine Überarbeitung der in diesen Leitlinien festgelegten Einleitkriterien wurde als wenig wirksam erachtet, da diese nur für neue Anlagen gelten würden.

In den kürzlich verabschiedeten "Leitlinien für die Risiko- und Folgenabschätzung der Abwässer von EGCS" (Rundschreiben MEPC.1/Circ.899) wird empfohlen, vor der Festlegung lokaler oder regionaler Beschränkungsmaßnahmen eine Umweltrisikobewertung nach einem einheitlichen Ansatz durchzuführen. Diese Maßnahme wurde nicht mit hoher Wirksamkeit bewertet. Die Durchführung einer Risiko- und Folgenabschätzung ist zeit- und kostenaufwändig, was die Ausweisung von Einleitverbotsgebieten verzögern könnte. Außerdem gewährleistet diese Maßnahme keinen globalen Schutz, da sie von der Initiative einzelner Staaten abhängt, die Beschränkungen nur in ihren Hoheitsgewässern durchsetzen können.

Zusätzliche Maßnahmen werden daher als notwendig erachtet. Es besteht die Möglichkeit, neue Maßnahmen in der IMO zur Diskussion zu stellen. Die weltweit harmonisierte Aufforderung zu einem Einleitverbot in Küstengewässern und/oder Hoheitsgewässern wird als geeignete Maßnahme mit großer Schutzwirkung angesehen. Es erscheint möglich, dass sich in den relevanten IMO-Ausschüssen hierfür Akzeptanz findet und sich die Maßnahme zeitnah umsetzen lässt. Die Schifffahrtsindustrie ist mit Einleitbeschränkungen innerhalb der 12-Seemeilenzone bereits vertraut, so dass eine solche Maßnahme kein Novum darstellen würde. Ein Nachteil dieser Maßnahme könnte sich ergeben, wenn das im Sammeltank gespeicherte Wasser aus dem CL ‚Zero Discharge'-Modus in der Nähe der Grenzen der Einleitverbotsgebiete eingeleitet wird, was dort das Risiko von Schadstoff-Hotspots erhöhen könnte. Ergänzend könnten als Maßnahme moderate Abflussraten für das gespeicherte Wasser empfohlen werden.

Bei der Bewertung potenzieller Schutzmaßnahmen ist es wichtig, den bestehenden umweltrechtlichen Rahmen, den voraussichtlichen Zeitrahmen für die Umsetzung und die Frage, ob die Maßnahmen auch für bestehende Anlagen gelten, zu berücksichtigen.

Fazit

Die in dem vorliegenden Bericht dargelegten Ergebnisse wie auch die Ergebnisse aus anderen Studien deuten darauf hin, dass die Scrubber-Abwassereinleitung potenziell schädliche Auswirkungen auf die Meeresökosysteme hat. Weitere Studien und Modelle können dazu beitragen, die Auswirkungen auf die Meeresumwelt besser zu verstehen. Es wird jedoch empfohlen, empfindliche und/oder stark verschmutzte Gebiete wie die Ostsee schnellstmöglich durch Einleitverbote zu schützen.

Die Diskussion über Schutzmaßnahmen bezüglich Scrubber-Abwasser muss dringend in den zuständigen Ausschüssen auf internationaler, regionaler und nationaler Ebene weitergeführt werden. Abschließend betrachtet ist die Nutzung von Scrubbern auch als Übergangstechnologie fragwürdig. Insbesondere mit Blick auf den Klimaschutz sollte der Einsatz von alternativen Kraftstoffen vorangetrieben werden, was wiederum den Einsatz von Scrubbern schrittweise beenden würde.

1 Introduction

1.1 Background

In order to reduce sulphur oxides (SOx) and particulate matter emissions from sea-going ships, regulation 14 of Annex VI of the International Convention for the Prevention of Pollution of Ships (MARPOL) sets out sulphur limits in fuel oil used on board ships. As an alternative, exhaust gas cleaning systems (EGCS), commonly referred to as 'scrubbers', may be operated on board to reach at least equivalent SOx emission reductions, while still using non-compliant fuels as allowed under regulation 4 of MARPOL Annex VI. The implementation of the sulphur limit in Emission Control Areas (ECAs) (0.1 %) in 2015 and of the global sulphur limit (0.5 %) in 2020 has boosted the development of the scrubber market in the maritime sector.

Scrubbers are classified in wet and dry scrubbers depending on the type of cleaning medium. In a wet scrubber, water (cleaning medium) is pumped into an absorption tower and sprayed into the exhaust gas stream. In the absorption tower, SOx are transferred very efficiently from the gas to the liquid phase, but also other pollutants from the exhaust gas such as heavy metals, oil residues and polycyclic aromatic hydrocarbons (PAH) end up in the water. Dry scrubbers, which make use of packed bed granulated chemicals, are not significantly present in the maritime sector and are not handled in this report, hence the term scrubbers used in this report refers only to wet scrubbers.

Seawater is commonly used in scrubbers. After the scrubbing process the water is usually released back to the sea. Depending on the mode of operation scrubbers can be classified in open loop (OL), closed loop (CL) and hybrid systems. Despite what the term 'closed loop' might infer, CL operation also generates wastewater (so called 'bleed-off'), which is usually discharged into the sea. For further information about the technical description of scrubbers refer to Marin-Enriquez et al. (2021).

There are environmental concerns regarding the discharge of scrubber water into the marine environment. This has been a subject of discussion at the Marine Environment Protection Committee (MEPC) and other subcommittees of the International Maritime Organization (IMO). In section 10 of the Guidelines for Exhaust Gas Cleaning Systems ('EGCS Guidelines') discharge criteria have been defined which were intended to prevent acute effects occurring in the aquatic environment (GESAMP, 2009). However, the amount of data of potential environmental adverse effects available at that point was scarce and it is questionable whether these criteria can ensure protection of the marine environment in the long run.

Addressing the need to generate the necessary knowledge about the characteristics of scrubber discharge water, the German Federal Maritime and Hydrographic Agency (BSH) carried out a project (2016-2019, Project No. (FKZ) 3716 51 101 0) on behalf of the German Environment Agency (UBA). The aim was to chemically characterize discharge water samples of five vessels equipped with scrubbers and model the emission and distribution of the scrubber discharge water in the Baltic and North Sea. The project report (Schmolke et al., 2020) stated that further research is needed for a better quantification and evaluation of the total impact on the marine environment of this abatement technology.

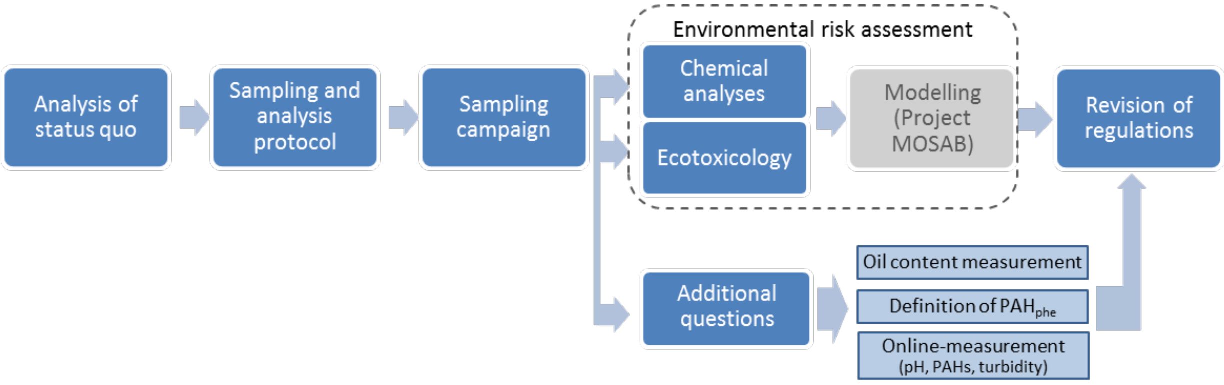
1.2 Project description and outline of this report

The follow-up project 'ImpEx – Environmental Impacts of Exhaust Gas Cleaning Systems for Reduction of SOx on Ships' (2020–2023, Project No. (FKZ) 3719 57 101 0) was carried out by BSH on behalf of UBA with the following cooperation partners: Federal Institute of Hydrology

(BfG), Hamburg Institute for Hygiene and Environment (HU), Hamburg Ministry of Environment, Climate, Energy and Agriculture (BUKEA), Helmholtz-Zentrum hereon GmbH (HEREON), UBA, University of Muenster (WWU) and Brigitte Behrends as consultant.

The project was focused on the analyses of scrubber discharge water and the evaluation of the current IMO scrubber-related regulation. Figure 1 displays the structure and main activities of the project.

Figure 1: Project structure and activities



'Modelling (Project MOSAB)' refers to a related project.

The project started with the analysis of status quo with special focus on the environmental aspects of the discharge water. It was based on a literature review and covered scrubber technical aspects, a market analysis, the regulatory framework and recent research activities related to this topic. The results of this activity were already published (Marin-Enriquez et al., 2021). Updated figures of the market analysis based on the information of the GISIS database can be found in Appendix A.

A sampling and analysis protocol (SAP) was developed and subsequently applied to the sampling and analysis campaign, which was aimed at determining the chemical composition and assessing the ecotoxicological effects of scrubber discharge water. The SAP is available as "Supplement A: Sampling and analysis protocol within ImpEx campaign" (see Appendix C) and complements Chapter 2 of the present report that presents the methods followed during the sampling and analysis campaign including information about the sampled ships and systems.

The results are reported and discussed under Chapter 3 of this report. Chapter 3 also includes the calculated emission factors and an evaluation of the water treatment efficiency in scrubber systems. The results will also serve as input for the related project MOSAB (Project No. (FKZ) 3721 57 103 0), which focuses on modelling of the distribution of discharge water and pollutants from scrubber in the marine environment especially in the North Sea and Baltic Sea. In this report, special emphasis is given to the results of the inlet and discharge water samples for certain parameters that are essential for the environmental assessment. 'Supplement B: Results of chemical characterization'[3] includes the complete results related to the chemical analyses of all samples.

Additional questions that are mainly related to the issues on the discharge water monitoring are addressed in sections 3.4 and 4.2.

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[3] Supplement B can be downloaded from the website: https://www.bsh.de/DE/THEMEN/Forschung_und_Entwicklung/Abgeschlossene-Projekte/_Anlagen/Downloads/sicherheit-und-umweltschutz/ImpEx_final_report_supplement_B.html.

As stated above, the evaluation and revision of the regulations related to scrubber discharge water was a main task within ImpEx. Section 4.3 contains the results of this evaluation.

In addition, the activities and developments on scrubber discharge regulation within the relevant international committees were followed during the project duration. Finally, a workshop and a final conference were organized within the framework of ImpEx; their findings were considered in this report.

2 Methods

A sampling and analysis campaign was conducted within the project to gain information about the chemical composition and ecotoxicological effects of scrubber discharge water. The sampling campaign included the single sampling of scrubber water, fuel oil and lube oil on board four ships (i.e. four samplings). The samples were delivered to several laboratories for the different analyses, while some parameters were measured on board.

A SAP was developed to provide the procedures for sampling and analysis of water from the scrubber system as well as of fuel and lubricating oil in order to preserve quality assurance and quality control, to ensure reproducibility within the campaign and to reduce possible uncertainties with regard to the results. The protocol was provided in advance to the ship operators as well as ship agencies collaborating in the project for the organization of the sampling. Before, during and after every sampling, technical documentation and relevant supporting data were collected. It should be noted that the SAP takes into consideration the guidance on discharge water data collection provided in the '2021 EGCS Guidelines' (resolution MEPC.340(77)) and the general principles of the standard ISO 5667-1, as appropriate. See Appendix C – Supplement A.

2.1 Sampled ships and systems

Table 1 contains the main supporting sampling data including details on ships and scrubber systems. In total four ships were sampled: two ferries for transport of vehicles and passengers (RoPax), one vehicles carrier and one cruise ship. The selection of the sampled ships was based mainly on their schedule and the scrubber type installed.

Every sampling entailed a voyage of a few days, however every sampling point was sampled a single time. The timely delivery of the water samples to the laboratories according to the SAP was the greatest challenge for the planning of the samplings. The samplings were conducted in the Baltic Sea and North Sea, hence there were brackish and saline seawater conditions, respectively (refer to Table 9 for the salinity of water samples). Ships equipped with scrubber hybrid systems were chosen to take water samples from both operation modes: OL and CL.

Engine type (2-stroke or 4-stroke) and type of installation (retrofit or newbuilding) can influence the concentration of organic pollutants in the exhaust gas and consequently in the discharge water. The combustion efficiency of the engine, which influences the concentration of organic pollutants in the exhaust gas, can be affected by the exhaust gas backpressure caused by the type of installation. For retrofits the selection of the scrubber is more challenging to fit to the existing engine and to avoid high backpressure.

The scrubber design might also affect the quality of the discharge water. I-type scrubbers are integrated into the exhaust funnel and require high water flowrates; whereas U-type scrubbers, installed outside the exhaust funnel, minimize water consumption as well as pressure drop and, due to the external venturi the removal rate for particulate matter from the exhaust gas could be enhanced. Both types can differ in the construction material as they required different temperature resistance. While the exhaust gas can flow through the I-type scrubber during shut-off (dry mode) and be exposed to higher temperatures, this is not possible in the U-type and the exhaust gas is by-passed in that case. Moreover, the U-type can have a packed bed. It should be noted that previous studies (Grubb and DeForce, 2018; Hermansson et al., 2021) have indicated the potential corrosion and abrasion of the scrubber material itself that could be a source of metals found in the discharge water.

Table 1: Relevant supporting sampling data

Parameter	Sampling 1	Sampling 2	Sampling 3	Sampling 4
Sampling date	12/2020	03/2021	08/2021	09/2021
Sampling region	Baltic Sea (Arkona Basin)	Baltic Sea (Bay of Pomerania)	North Sea (Frisian Front)	North Sea (German Bight)
Ship type	Ferry (RoPax)	Ferry (RoPax)	Vehicles carrier	Cruise ship
Engine type	4-stroke	4-stroke	2-stroke (ME) 4-stroke (AE)	4-stroke
Type of installation	Retrofit	Retrofit	Newbuilding	Newbuilding
Scrubber design	I-type	U-type	U-type	U-type
Scrubber type	Hybrid (OL, CL)	Hybrid (OL, CL)	Hybrid (OL, CL)	Hybrid (OL, CL)

AE: Auxiliary engine; CL: Closed loop; ME: Main engine; OL: Open loop.

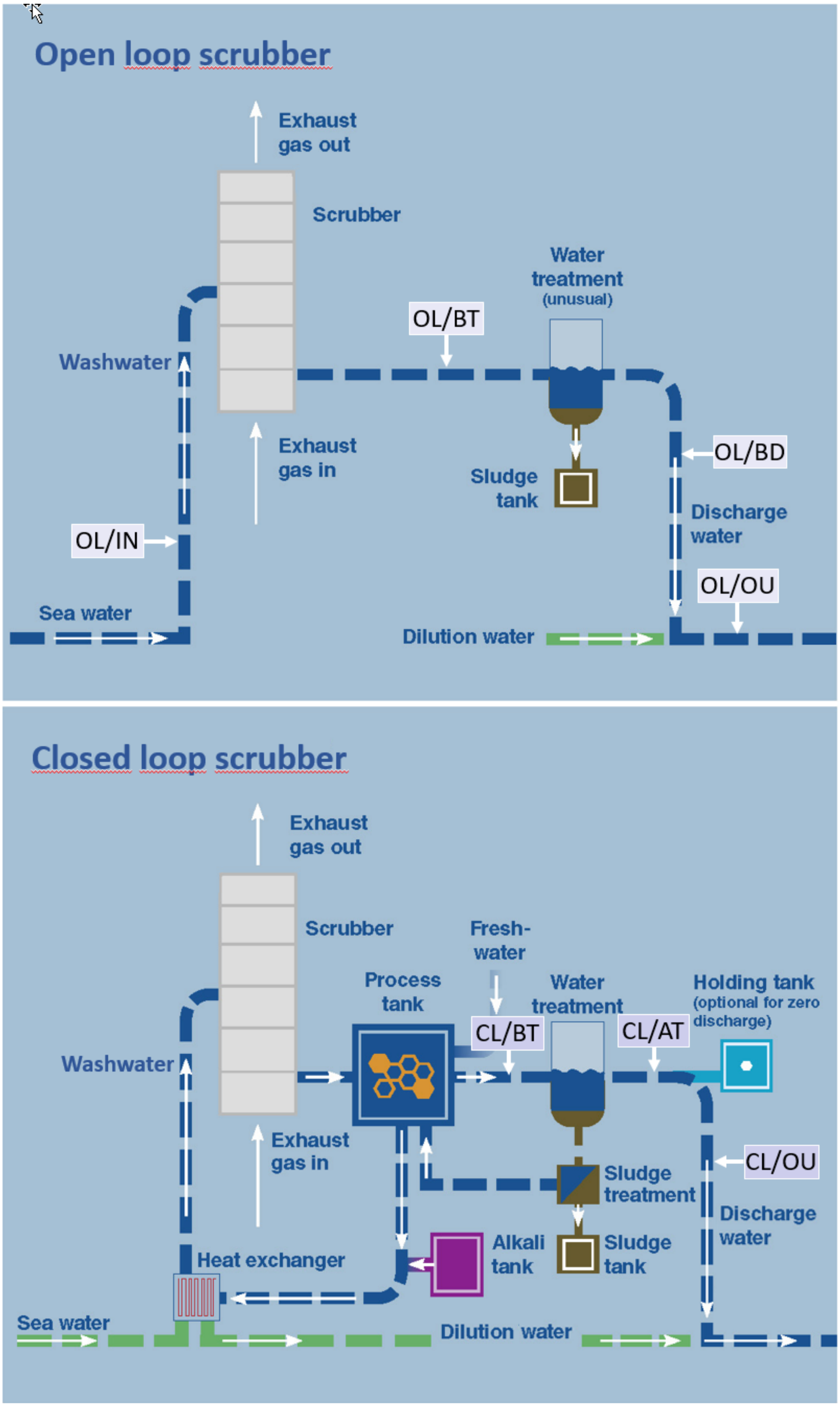
2.2 Sampling of water samples

The sampling of water samples was conducted by trained project's personnel according to the SAP. As mentioned above, the scrubber systems were sampled one time each in both operation modes: OL and CL. The recommended sampling points of the drafted '2021 EGCS Guidelines' were considered for the sampling programme. In order to evaluate the potential environmental impact, the focus was on the sampling of discharge water. Additional water streams, part of the scrubbing process, were sampled to determine the enrichment and origin of pollutants as well as the efficiency of water treatment units (if provided). Figure 2 shows the targeted water streams to be sampled in both operation modes. Although bleed-off water after treatment (CL/AT) and bleed-off outlet water (CL/OU) in CL operation mode might have a similar composition (no operation unit in between), sampling of these water streams followed different purposes. CL/AT represents the water conditions at a very specific moment (like a 'snapshot') and their results were compared to bleed-off before treatment (CL/BT) to determine the water treatment efficiency. CL/OU is discharge water from the holding tank after storage (prior to any dilution) representing a whole CL operation (e.g. during a port stay) and these results should be considered for the environmental impact assessment.

For the determination of the sampling points on every ship an inspection of the scrubber system and pipelines was conducted to ensure representativeness of the targeted water streams, accessibility to personnel and fulfilment of further requirements specified in the SAP such as cleanliness and suitability of materials of the sampling points. Any deviation from those requirements was properly documented. For some targeted water streams there were deficient sampling points and even no existing sampling points. This issue is discussed in section 4.2. Further procedures for the collection, storage, transportation and documentation of the samples are described in the SAP.

Table 2 summarizes the sampling points covered in every sampling and the sampling codes employed. The scrubber of ship 4 did not require dilution water in OL operation. Thus, the sampling point after the water treatment can be considered as both, water stream before dilution (OL/BD) and outlet (OL/OU). Only here the sampling of the OL water stream before treatment (OL/BT) was possible.

Figure 2: Location of sampling points in OL (top) and CL (bottom) operation modes



Sampling codes as described in Table 2. Source: BSH (2022).

Table 2: Sampling points programme per sampling

Sampling code	Short description	S1	S2	S3	S4
OL/IN	OL-inlet	X	X	X	X
OL/BT	OL-before treatment				X
OL/BD	OL-before dilution	X	X	X	X
OL/OU	OL-outlet	X	X	X	
CL/BT	CL-before treatment	X	X	X	X
CL/AT	CL-after treatment	X	X	X	X
CL/OU	CL-outlet	X	X	X	X

S1 – S4 refer to the sampled ships. Ship 4 did not require dilution water in OL operation. Thus, the sampling point after water treatment can be considered as both OL/BD and OL/OU.

Information about the operating conditions of the engines and the scrubber system during sampling was collected (Table 3).

The sampling in OL mode was conducted under stable operating conditions (especially for engine load and washwater flow) and during normal transit conditions. Preferably the scrubber should operate above 50 % of its maximum capacity or the engine load above 50 % of aggregated maximum continuous rating of all fuel oil combustion units connected to the scrubber. The sampling schedule was agreed with the ship's personnel considering these requirements. The specific flowrates during OL mode sampling were 54 – 93 m^3/MWh (see Table 3). They were obtained by dividing the washwater flowrate (without consideration of dilution water) by the accumulated average engine load of the combustion units connected to the scrubber and operated during the sampling period. The flowrate of the dilution water is reported separately. Only ship 1 reported this parameter based on online measurements. Ships 2 and 3 did not measure this parameter so that the reported values are estimations from the ship's personnel based on the capacity and efficiency of the water pumps. Ship 4 did not require dilution water prior to discharge. Ships 2 - 4 were equipped with and operated a hydrocyclone for water treatment prior to discharge.

The sampling from CL operation could not be conducted surely under stable operating conditions due to the complexity of the system and the normal variable operating conditions. The CL mode in hybrid systems is usually operated during transit (close to port), manoeuvring and berthing (in port). Because the washwater in CL operation is re-circulated inside the system, the bleed-off represents a mixture of the last operation hours. Some systems are controlled to take bleed-off from the process (or recirculation) tank when the density of the water reaches a pre-set value to prevent the precipitation of accumulated salts. The samples of the discharge from the holding tank (CL/OU) were actually taken during operation of OL mode, during transit and outside areas with local discharge bans. The discharges from CL operation took place mostly manually either after leaving or before entering an area with a discharge ban depending on the system requirements (capacity level of holding and process tank) and availability of ship's personnel. The volume capacity of the holding tanks in the sampled ships ranged from 42 to 250 m^3.

For ships with hybrid scrubber systems, it seems to be a common practice to mix the discharge from the holding tank (CL/OU), namely the stored treated bleed-off water from the CL operation, with the discharge water from the OL operation before discharging it into the sea.

Notwithstanding this practice, the present study assessed the discharge water from the CL operation separately from the OL discharge water in order to determine the chemical characterisation and ecotoxicological effects of these two different wastewater streams and to be able to compare the operation modes. These results (attributed to a specific energy output) can thus be used for environmental risk assessments considering emission scenarios with all types of scrubber systems: OL, CL and hybrid. The assessment of a mixed discharge from CL together with OL discharge water is not suitable for this purpose as the assignation of the pollutants load and ecotoxicological effects to a specific energy output and the respective scrubber operation mode (OL and CL) would be practically impossible. Moreover, previous studies that included sampling of scrubber systems have followed a similar sampling approach (e.g. EGCSA & Euroshore, 2018; Hansen, 2012; Kjølholt et al., 2012), which has been recommended by scrubber manufacturers (EGCSA & Euroshore, 2017).

In Table 3, the reported CL-engine load is the accumulated average load of the engines connected to the scrubber and operated during the period estimated to cover the CL operation that generated the water in the holding tank (e.g. port stay prior to discharge). The combined range of discharge flowrate (2.2 – 8.6 m^3/h) was obtained from records (if provided) and estimations provided by ship's personnel. This range, however, was not used to calculate the specific flowrates due to the variability of the operating conditions and complexity of the CL mode (e.g. delayed discharge) as well as the insufficient information and records. Instead, the accumulation of sulphur in the bleed-off water (see Table 9 for sulphur concentration in water samples and Table 14 for fuel sulphur content) was used to estimate the specific flowrates in CL operation that ranged from 0.20 to 3.5 m^3/MWh. These values are 15 to 360 times lower than the specific flowrates in OL mode. The specific flowrates reported in Table 3 were used to calculate emission factors (mass load of pollutant per energy output, see section 3.2) of different pollutants based on the results of the chemical analyses. The specific fuel oil consumptions (SFOC) together with the results of the fuel oil composition (see Table 14) were used to calculate the maximum potential pollutant load per energy output from the fuel (see Table 15).

Table 3 specifies the bleed-off treatment units of every ship. Centrifugal separator and dissolved air flotation were used as treatment technologies in CL operation in the sampled ships; these technologies are commonly reported in the literature (Marin-Enriquez et al., 2021). Two ships made use of flocculants and coagulants to enhance the water cleaning efficiency: polyacrylamide (S1 and S4) and polyaluminium chloride (S4). Ships S1-S3 reported use of seawater for CL operation, while ship S4 made use of freshwater.

Table 3: Operating conditions during sampling

Parameter	S1	S2	S3	S4
OL-Specific flowrate (m^3/MWh) [i.]	**93**	**54**	**67**	**72**
OL-Washwater flowrate (m^3/h)	952	622	732	815
OL-Dilution flowrate (m^3/h)	106	~300	~550	0
OL-Engine load (%)	75	86	63	79
OL-Engine load (MW)	10.2	11.6	11.0	11.3
SFOC during OL sampling (kg_{fuel}/MWh)	212 [ii.]	217 [ii.]	164 [iii.]	219 [ii.]
OL-Water treatment	-	Hydrocyclone	Hydrocyclone	Hydrocyclone

Parameter	**S1**	**S2**	**S3**	**S4**
CL-Specific flowrate (m^3/MWh) [iv.]	**3.0**	**3.5**	**0.35**	**0.20**
CL-Discharge flowrate (m3/h)	2.2 – 8.6 m^3/h [v.]			
CL-Engine load (%)	22.3	15.6	37.6	36.9
CL-Engine load (MW)	4.5	2.1	8.0	12.4
SFOC during CL sampling (kg_{fuel}/MWh)	225 [iii.]	231 [iii.]	168 [iii.]	209 [ii.]
CL-Bleed-off treatment	Centrifugal separator with flocculant addition	Centrifugal separator	Centrifugal separator	Dissolved air flotation with flocculant addition

CL: Closed loop; OL: Open loop; SFOC: Specific fuel oil consumption.

i. Calculated based on 'OL-Washwater flowrate (m^3/h)', without consideration of dilution water, and 'OL-Engine load (MW)'.
ii. SFOC calculated based on fuel consumption rate data and actual engine load.
iii. SFOC estimated considering ship-specific typical values during a cruise (at full load) for OL and at port (at lower load) for CL reported in operation manual or provided by ship's personnel.
iv. Estimated based on the accumulation of sulphur in the bleed-off water and the fuel sulphur content.
v. Combined range based on records and estimations provided by ship's personnel, when discharge rate is not measured. This range was not used to calculate the specific flowrate.

2.3 Chemical analyses on scrubber water samples

2.3.1 Measurements on board

Measurements of parameters on board were conducted by trained project staff by means of portable devices and a mobile measuring cabinet (see Table 4). The portable devices (Hach-turbidimeter and Hanna-multiparameter HI98195) were used for the measurement of pH, temperature, conductivity and turbidity immediately after sampling. During the first sampling the turbidimeter was not available.

A measuring cabinet EGC Water Analyzer (TriOS) equipped with sensors for measurement of pH, temperature, turbidity and polycyclic aromatic hydrocarbons (as phenanthrene equivalent, PAH_{phe}), together with a spectral sensor OPUS-UV (TriOS) for measurement of nitrate and nitrite were assembled into a mobile frame and integrated into a measuring system loop for additional measurements on board (see SAP for further details). In order to enable the execution of the sampling schedule, water samples from every sampling were collected and measured in series instead of measuring after sampling of every single sampling point as suggested in the SAP. The measurements on S1 and S2 were conducted a few hours after the sampling. The mobile measuring equipment could not be brought on board S3 and S4 due to logistic impediments. Hence, the measurements were delayed by one day (S4) and three days (S3). However, measurements of pH, temperature and turbidity were carried out immediately after the sampling with the portable devices (see Table 9). Unlike these parameters, a relatively short delay (one to three days) in the measurement of PAH_{phe} is less critical. It should be noted that there were no requirements for the preservation or stabilisation of these samples.

The results of the measurements on board are compared to the values reported from the onboard online monitoring data from the ship (see section 3.4.1). Additionally, the measured values for PAH_{phe} were compared with the laboratory results for phenanthrene, sum of 16 EPA PAH and oil content to evaluate the correlation between these parameters (see section

3.4.2). Further, the measured values for nitrogen compounds were compared with the laboratory results to evaluate the technical feasibility for online monitoring of these parameters in scrubber discharge water (see section 3.4.3).

Table 4: Parameters measured on board and measuring devices

Parameter	Sensor and standard	Device (manufacturer)
pH	HI7698194-1, N/A	Portable device, multiparameter HI98195 (Hanna, Romania)
Temperature	N/A, N/A	
Conductivity	HI7698194-3, N/A	
Turbidity	N/A , ISO 7027	Portable device, turbidimeter 2100Qis (Hach, China)
pH	TpH-D, DIN EN 60746-2:2003-09	Measuring cabinet, EGC Water Analyzer (TriOS, Germany)
Temperature	TpH-D, N/A	
Turbidity	TTurb sensor, DIN EN ISO 7027-1:2016-11	
PAH_{phe}	enviroFlu, MEPC.184(59)	
Nitrogen compounds	OPUS-UV, N/A	

N/A, Not available; PAH_{phe}, Polycyclic aromatic hydrocarbons – phenanthrene equivalent.

2.3.2 Laboratory analyses

The water samples were analysed to determine their chemical composition by the laboratories of HU, the Institute of Geology and Palaeontology of WWU and HEREON. The measured parameters included general parameters (i.e. pH, alkalinity, suspended solids, total organic carbon and dissolved organic carbon and sulphur), nitrogen compounds, metals, organic compounds (i.e. PAH, oil content as hydrocarbon oil index, volatile organic carbons, dioxins and polychlorinated biphenyls) and non-target screening of PAH. Most of the parameters were determined by HU, except for the extended list of PAH and the GC-MS screening for non-target polyaromatic compounds by WWU as well as the determination of metals with lower limit of quantification by HEREON.

Table 5 contains the list of the measured parameters and the followed standard methods. For the determination of the parameters in the dissolved form water samples were generally filtered (0.45 µm), only for the determination of the extended list of PAH the samples were centrifuged (18000 G for 30 min). Further details regarding the analysis methods and procedures are found in the SAP. For certain parameters only samples from selected ships and water streams were analysed (as indicated in Table 5).

Previous studies on scrubber discharge water (Linders et al., 2019; Magnusson et al., 2018) have indicated the presence of PAH (e.g. alkylated PAH) other than the usually measured 16 EPA PAH that contribute to the mixture toxicity. To collect further information in this regard, it was decided to include the analysis of an extended list of PAH that includes about 70 different compounds (including the 16 EPA PAH). Similarly, a non-target screening (qualitative analysis) was included in the scope of analyses to identify potential further other unknown polyaromatic organic compounds in the discharge water.

Additional analyses of metals with lower limits of quantification (than originally measured by HU) were considered for selected OL water samples to better evaluate the enrichment of metals in the discharge water and to compare the quality of the inlet water with the typical environmental concentration in the water of the sea region. HEREON conducted the additional analyses of metals with methods appropriate for metal trace analysis in seawater samples. Because these analyses were not originally planned, the water samples of S1-S3 provided to the laboratory were stored for a long time at room temperature and without conditioning. However, as metals cannot be degraded and may only change their oxidation state as well as their dissolve/particulate status it was decided to analyse these samples anyway.

Table 5: Chemical parameters measured at the laboratories and their analysis method

Parameter	Analysis method
pH	DIN EN ISO 10523:2012-04
Alkalinity	DIN 38409-7:2005-12
Suspended solids	DIN EN 872:2005-04
Total organic carbon (TOC)	DIN EN 1484: 1997-08
Dissolved organic carbon (DOC)	DIN EN 1484: 1997-08
Total nitrogen bound (TNb)	DIN EN 12260: 2003-12
Nitrate	DIN EN ISO 13395:1996-12 (CFA- Continuous flow analysis)
Nitrite	DIN EN ISO 13395:1996-12 (CFA- Continuous flow analysis)
Sulphur	DIN EN ISO 11885:2009-09 (ICP-OES)
Metals [As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, Zn] [Hg]	DIN EN ISO 17294-2:2017-1 (ICP-MS/MS) DIN EN ISO 12846:2012-08 (CV-AAS) If required: DIN EN ISO 17852:2008-04 (CV-AFS)
Metals (dissolved) [Cd, Cu, Fe, Mn, Ni, Pb, Ti, V, Zn, other heavy metals, metalloids and rare-earth elements] [ii.]	In-house method (ICP-MS/MS coupled to seaFAST SP2) [i.]
Metals (dissolved) [As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, Zn] [Hg] [ii.]	ISO 17294-2:2017-1 (ICP-MS/MS) ISO 12846:2012-08 (CV-AAS) If required: ISO 17852:2008-04 (CV-AFS)
16 EPA PAH	DIN 38407-F39: 2011-09 [iii.]
Indicator PCB [ii., iv.]	DIN EN ISO 6468: 1997-02 DIN 38407-37:2013-11
GC-MS Screening [ii.]	DIN 38407-F39: 2011-09 (NIST-Data base)
16 EPA PAH (dissolved)	DIN 38407-F39: 2011-09 [iii.]
Indicator PCB (dissolved) [ii., iv.]	DIN EN ISO 6468: 1997-02 DIN 38407-37:2013-11

Parameter	Analysis method
GC-MS Screening (dissolved) ii.	DIN 38407-F39: 2011-09 (NIST-Data base)
Non-targeted analysis (dissolved and particulate) ii., v.	In-house method (GC-APLI-MS) vii.
HOI	DIN EN ISO 9377-2: 2001-07
HOI (dissolved)	DIN EN ISO 9377-2: 2001-07
VOC (HVHH/BTEX) ii.	DIN 38407-43: 2014-10 vi.
Dioxins (PCDDs/PCDFs) ii.	ISO 18073:2004-04
Dioxins (PCDDs/PCDFs) (dissolved) ii.	ISO 18073:2004-04
Extended list of PAH (dissolved) ii., v.	In-house method PAK104_RESTEK (GC-MS) vii.
Extended list of PAH (particulate) ii., v.	In-house method PAK104_RESTEK (GC-MS) vii.

Abbreviations: 16 EPA PAH, Priority PAH listed by the US Environmental Protection Agency; AAS, Atomic absorption spectrometry; AFS, Atomic fluorescence spectrometry; APLI, Atmospheric-pressure laser ionization; As, Arsenic; BTEX, Benzene, toluene, ethylbenzene and xylene; Cd, Cadmium; Co, Cobalt; Cr, Chromium; Cu, Copper; CV, Cold vapor; Fe, Iron; Ga, Gallium; GC, Gas chromatography; Hg, Mercury; HOI, Hydrocarbon oil index; HVHH, Highly volatile halogen hydrocarbons; ICP, Inductively coupled plasma; Mn, Manganese; MS, Mass spectrometry; Ni, Nickel; OES, Optical emission spectrometry; PCB, Polychlorinated biphenyl; PCDDs/PCDFs, Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; Pb, Lead; Sb, Antimony; Ti, Titanium; V, Vanadium; VOC, Volatile organic compounds; Y, Yttrium; Zn, Zinc.

i. HEREON in-house method KBA_0031_seaFAST_SP2. It includes the use of an automated pre-concentration system for undiluted seawater or other high matrix samples (seaFAST SP2).
ii. Analyses were not carried out in all samples.
iii. The national norm DIN 38407-F39: 2011-09 is very similar to the international norm ISO 28540.
iv. Indicator PCB: CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180.
v. Separation of dissolved and particulate phases by centrifugation (see SAP).
vi. Annex 7 of SAP includes the list of the determined volatile organic compounds.
vii. As described in Annex 6 of SAP.

2.4 Ecotoxicity testing on scrubber water samples

For the ecotoxicological assessment of the scrubber water samples a combination of whole effluent toxicity (WET) tests on two marine planktonic species as well as luminescent bacteria and two specific tests for genotoxic and dioxin-like effects was selected. To supplement this test battery by an aquatic vertebrate species, acute toxicity of samples to zebrafish eggs were included. WET tests and fish egg test represent organisms of four different trophic levels. Table 6 lists the conducted biotests and the corresponding standard methods.

Table 6: Ecotoxicological assays and their analysis method

Biotests	Test organism and standard method
Luminescent bacteria test (WET)	*Aliivibrio fisheri* (DIN EN ISO 11348-2:2009-05)
Marine algal growth inhibition test (WET)	*Phaeodactylum tricornutum* (ISO 10253:2006)
Marine copepods acute lethal toxicity test (WET)	*Acartia tonsa* (ISO 14669:1999)

Biotests	Test organism and standard method
Recombinant yeast assay (hAHR-binding): (Dioxin-like effect)	Recombinant yeast cells *Saccharomyces cerevisae* (method according to Miller *et al.* 1999 and following the principles of ISO 19040-1)
Ames fluctuation test (mutagenic potential)	*Salmonella enterica* subsp. enterica serotype typhimurium (ISO 11350:2012) Used strains: TA98, TA100, YG1041 und YG1042
Zebrafish eggs acute toxicity test	*Danio rerio* (DIN EN ISO 15088:2009)

Abbreviations: hAHR, Human aryl hydrocarbon receptor; WET, Whole effluent toxicity.

The luminescent bacteria and marine algae WET tests were conducted by the contract research organization Institut Dr. Nowak, Ottersberg (Germany) on behalf of and coordinated by BfG. For quality assurance reasons, BfG performed these tests in parallel to the contract laboratory except for S1. The volumes of the samples obtained from the first ship were smaller and insufficient for additional testing at BfG. The samples volumes were subsequently increased to satisfy the higher demand. The copepods tests were conducted at the contract laboratory Noack, Sarstedt (Germany) only. BfG additionally conducted recombinant yeast assays and Ames tests using *Salmonella* strains TA98 and TA100. UBA performed Ames tests with strains YG1041 and 1042 as well as fish egg tests.

Figure 3 illustrates the testing procedures and depicts the conducted biotests. The water samples were divided across the laboratories for testing. For WET testing, samples were used native. For other tests, extraction was required to concentrate and desalt the samples. For very turbid samples, a filtration step (type A/C glass fibre membrane filter, 1.0 µm pore size; Pall Corp.) was included prior to WET testing to remove suspended and precipitated particles from the samples, which could otherwise interfere with the bioassay performance. It should be noted that pollutants can be particulate-bound. This fraction of pollutants was removed from the samples by the filtration and thus excluded from the ecotoxicity test.

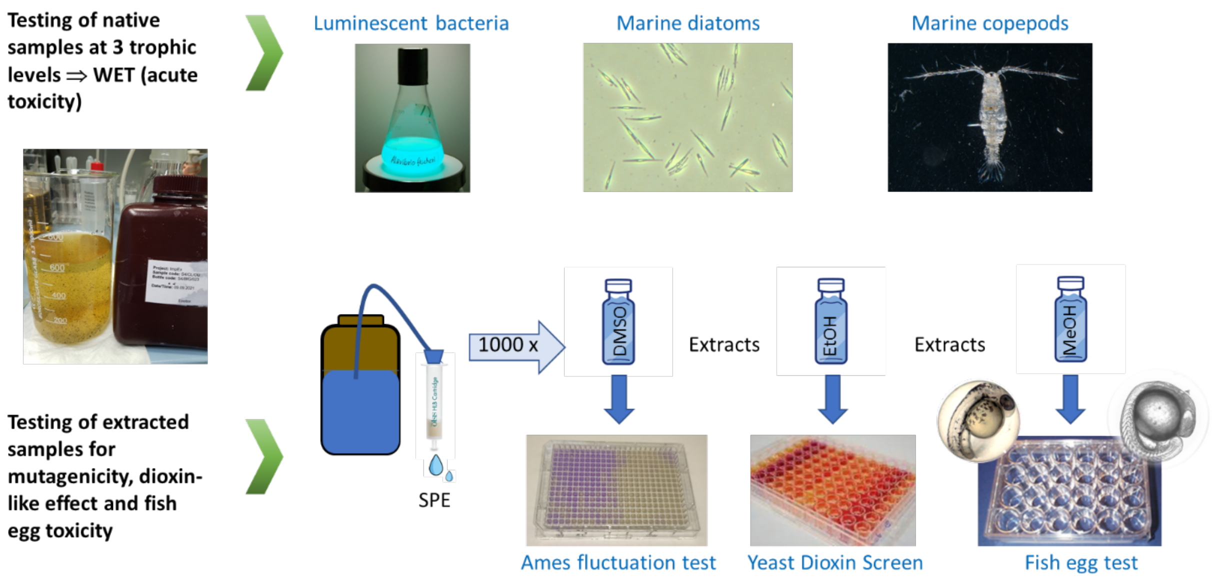
After filtration, a pH-adjustment to pH 7.0 was performed in case of deviations from the acceptable range between pH 6 and 8. The low pH of scrubber samples can have detrimental effects on organisms, thus adjusting the pH is required for conducting most bioassays. However, shifting the pH towards neutral can change the speciation of certain substances (e.g. metals) and thus change their bioavailability or cause precipitation.

Solid-phase extraction (SPE) of the samples was performed at BfG by means of reverse-phase SPE cartridges (Macherey-Nagel Chromabond "Hydrophilic-lipophilic balanced"- HLB, Ref. 730926). The HLB-SPE columns are designed for enrichment of substances of a broad range of polarities, with enhanced retention of polar compounds. Also, SPE removes the salt from the samples. The selection of the SPE-columns was based on a compromise because the physico-chemical properties of the contaminants of scrubber water samples are too broad to be retained by just one type of resin. A mixed-mode SPE approach (e.g. through combination of reverse-phase and ion-exchange resins) may have improved the extraction, in particular of inorganic components.

For the extraction, the samples were subjected to the SPE-columns and subsequently eluted from the columns using 100 % methanol to achieve 1000-fold concentrated samples. Since methanol was not compatible with the yeast and Ames *in-vitro* bioassays, the methanol was evaporated and exchanged by dimethyl sulfoxide (DMSO) for the Ames test and by ethanol for the yeast assay (volume according to the targeted enrichment factor of 1000) prior to testing.

Methanol as solvent was only used in the fish egg tests. The details of the extraction protocol are found in the SAP.

Figure 3: Schematic workflow of the ecotoxicity assessment



Abbreviations: DMSO, dimethyl sulfoxide; EtOH, ethanol; MeOH, methanol; SPE, solid-phase extraction; WET, whole effluent toxicity. Source: BfG (2022); UNIFISH-group (Fraunhofer IME) has the copyright of the fish embryos images.

2.4.1 Whole effluent toxicity tests

The Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) Task Team on scrubber discharges advised to generate further information on direct ecotoxicological effects through well-established WET tests (Linders et al., 2019). Other than a single substance-based approach, WET testing (US EPA, 2002) allows to evaluate the aggregate toxic effects to aquatic organisms from all contaminants contained in a wastewater sample. This approach is used in national and international environmental policy frameworks for discharge of wastewaters. For instance, the OSPAR Commission developed a guidance document on Whole Effluent Assessment (OSPAR, 2007) and specifically highlights the above-mentioned advantage to overcome the shortcomings of the 'single substance approach', especially when assessing combined effects of complex mixtures. WET tests can be applied to determine acute as well as the chronic effects on survival, growth and reproduction of aquatic tests organisms representing different organism groups of different trophic levels. ImpEx focused on short-term acute WET tests.

The WET tests were performed in compliance with the international standards listed in Table 6 and passed all validity criteria as outlined in the corresponding standard. The test organisms comprised luminescent bacteria (*Aliivibrio fisheri*), marine algae (*Phaeodactylum tricornutum*) and marine copepods (*Acartia tonsa*), which represent the trophic levels of decomposer, primary producer and primary consumer, respectively. The details of the WET test methods and their procedure can be found in the corresponding DIN-ISO-standard documents.

The principle of WET testing stipulates not to alter the water samples or to keep necessary adjustments to a minimum. Thus, the physico-chemical and particulate properties of the scrubber water samples were only adjusted in cases where the minimum requirements of the test organisms were not met. With both OL and CL samples, acidity could be an issue, with the CL-samples oxygen depletion, turbidity and particles had to be addressed. Turbidity and particles can adversely affect organisms, for instance by inhibiting photosynthesis in the algae or by distorting optical evaluations or measurements like fluorescence of algae or luminescence of bacteria. Furthermore, the salinity of the samples from the Baltic Sea (S1 and S2) was <20 PSU (practical salinity unit) and thus, had to be raised by addition of NaCl (Sigma-Aldrich) to ≥20 PSU to become compatible with the marine test organisms. For the marine algae, 20 PSU is sufficient whereas the copepods require at least 29 PSU. The luminescent bacteria are also marine organisms, therefore require a minimum salinity of 20 PSU. For salinity values above 35, no adjustments were made before testing luminescent bacteria and algae, thereby respecting that hyperosmotic effects in the test organisms may occur.

All water samples were serially diluted using a dilution factor of 2 and at least five dilutions tested for each WET test. As a measure of toxicity, the lowest dilution at which no significant test-specific effects were detected, the lowest ineffective dilution (LID), was determined (see Table 7). The LID is a toxicity threshold level comparable to the no-observed effect concentration (NOEC), although in the narrow sense the NOEC relates to chronic effects and to defined concentrations of a single substance rather than dilutions of a liquid environmental sample. LID is also not derived through statistically analysis of data (OSPAR, 2007).

In the context of the management of dredged material from federal waterways, the BfG uses the pT-method to assigns sediment, pore water and eluate samples to toxicity classes according to their pT-value (*potentia toxicologiae*). The pT-method was originally developed as a management tool to incorporate bioassay data in the decision-making process for assessing and comparing the relative toxic hazards of industrial effluents and was initially applied to industrial effluents in the Rhine river basin (Krebs 1988, 2005). In the context of ImpEx, this method was deemed suitable to also categorise the toxicity of the scrubber water samples and was applied to the WET-test results.

For this method, the pT-value should be obtained from at least three standard aquatic test organisms of three different trophic levels. The pT-value corresponds to the LID in each of the tests and is derived from the negative binary logarithm of the first not toxic dilution factor (see Table 7). The most sensitive test species of the test battery therefore has the highest pT-value (pT_{max}-value), which translates to a toxicity category between 1 and 6. This pT_{max}-value can be considered a measure of the toxicological potential of a sample. All $pT_{max}>6$ are also assigned to the toxicity category 6, which denotes extreme toxicity (Table 7).

Table 7: Classification of the ecotoxicological effect potential (adapted from Krebs, 2000 & BfG, 2020)

Dilution ratio	Lowest ineffective dilution (LID)	Proportion of original (y) in diluted sample	pT-value* (-log$_2$(y))	pT$_{max}$ and categorisation**	
Original		1.0	0	0	Non-toxic
1:2	2	0.50	1	1	Practically non-toxic
1:4	4	0.25	2	2	Slightly toxic
1:8	8	0.125	3	3	Moderately toxic
1:16	16	0.0625	4	4	Considerably toxic
1:32	32	0.0313	5	5	Highly toxic
1:64	64	0.0157	6	6	Extremely toxic
1:128	128	0.0078	7	6	Extremely toxic
…	…	…	…	6	Extremely toxic

*pT = *potentia toxicologiae*

**The toxicity category is determined by the most sensitive test (pT$_{max}$)

2.4.1.1 Luminescent bacteria

Luminescent bacteria test was conducted in compliance with DIN EN ISO 11348-2:2009-05. The test uses the marine luminescent bacterium *Aliivibrio fisheri* as test organism. *Aliivibrio fisheri* naturally emits bioluminescence which is linked to normal metabolic activity and energy production of the bacteria. Chemical exposure can impair the metabolism of the bacteria and consequently reduce or even inhibit the bioluminescence. The test measures the decrease of the bioluminescence after 30 min of exposure to a chemical or contaminated environmental sample in comparison to an unexposed control condition. For the test, the bacteria were exposed to a series of dilutions of the water samples in order to determine the effect threshold of 20 % inhibition of luminescence (EC$_{20}$) and thereby the LID just below this 20 %-threshold. A minimum of four dilutions were measured for the OL and five dilutions for the CL samples to achieve this goal. Since the bacteria need to be suspended in a culture and reactivation medium to become active and emit bioluminescence, 20 % of the test solution of each treatment consist of this medium, thus the lowest dilution of a samples is 80 %. For each dilution and the controls two replicates were used and for each replicate a test volume of 1.0 ml in a 3.0 ml glass cuvette was used. The negative control treatment was artificial sea water (20 or 30 PSU) and the positive control substance was 3,5-dichlorophenol (4.5 mg/l). The test is performed at 15 ± 0.1°C in a thermoblock (LUMIStherm, Hach). Bioluminescence intensity (I) of the bacteria was measured in all test vessels after an adapting phase of 15 min (I$_0$) and then after adding the sample 30 min later (I$_{30}$). The inhibition of bioluminescence (%) results from the difference between the mean intensities at I$_0$ and I$_{30}$, under consideration of a correction factor which accounts for the intrinsic loss of luminescence in the unexposed control bacteria. It should be noted that chemical exposure can also stimulate the bioluminescence, resulting in a negative inhibition effect. The bacteria used were liquid-dried and obtained from Hach (Germany) as LUMIStox - LCK 482 test kit, which also contains the reactivation medium.

2.4.1.2 Marine algae

The marine algal growth inhibition test was conducted in compliance with ISO 10253:2016. The unicellular marine algae *Phaeodactylum tricornutum* was used as test organism. Monospecies algal suspensions in the exponential growth phase were obtained by 3-day preculturing of algal inocula. A dilution series of the water samples was prepared with the algal growth medium and inoculated with a specific volume of the concentrated algal suspension to obtain a start density of 104 algal cells/ml. This series of dilutions of the water samples was tested in order to determine the effect threshold of 20 % inhibition of growth rate (EC_{20}) and thereby the LID just below this 20 %-threshold.

The test vessels were incubated for a period of 72 ± 2 h at a nominal temperature of 20 °C, under continuous white light. The temperature should not vary by more than 2 °C during the test. As apparatus for the test, a temperature-controlled cabinet was used. Inhibition of algal growth was measured by means of relative chlorophyll fluorescence in a spectrophotometer at 685 nm (excitation 435 nm) and expressed as a reduction of specific growth rate relative to control cultures, grown under identical conditions.

2.4.1.3 Copepods

The copepod test was conducted in compliance with ISO 14669:1999 E. Briefly, adult (or developmental stage 5) copepods were exposed to a series of dilutions of the water samples in order to determine the LID (effect threshold of 20 %) and the dilution at which 50 % of the exposed animals are killed after 48 h. This is the median lethal concentration LC_{50} (48 h). The test species used was *Acartia tonsa* and the animals were obtained from Guernsey Sea Farms Ltd. (Vale Guernsey, UK). The animals were acclimatised and cultured at the test facility at standard conditions for at least one week prior to the test start. The test was carried out at 20 ± 2 °C in 50 ml-glass beakers (test volume per vessel 25 ml) at a 16:8 h light:dark cycle in an incubator cabinet. For each dilution and the controls four replicates were used with five animals per replicate, thus 20 animals per treatment. The negative control treatment was artificial sea water and the positive control substance was 3,5-dichlorophenol (0.5 mg/l). The exposure was static. Mortality was recorded after 24 h and 48 h. The recommended salinity for the test species is 29 – 36 PSU. Thus, the salinity of samples from S1 and S2 was raised to 30 PSU using sea salt (Sigma-Aldrich) prior to test start. The CL samples of S3 and S4, however, showed salinities ≥50 PSU. These samples could therefore not be tested at 100 % (undiluted) and had to be diluted to at least 50 % (1:2).

The copepod testing was conducted by Noack Laboratorien GmbH in 31157 Sarstedt, Germany, on behalf of the BfG.

2.4.2 Specific-toxicity tests

In addition to the whole organism, acute ecotoxicity tests (WET and fish-egg tests), specific toxicity tests allow the investigation of specific effects of pollutants.

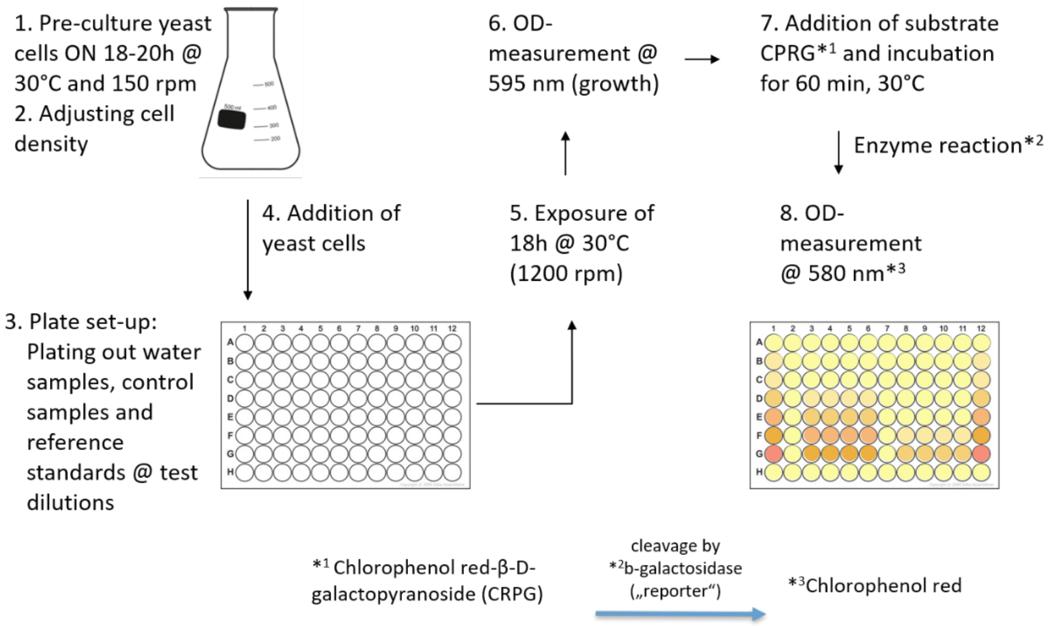
2.4.2.1 Yeast dioxin screening

The yeast dioxin screening (YDS) enables the investigation of the specific binding and activation of the aryl hydrocarbon receptor (AHR) by pollutants. Since in particular dioxins and dioxin-like compounds have a high affinity for this type of receptor, this is described as a dioxin-like effect.

The YDS is a so-called reporter assay with recombinant yeast cells (*Saccharomyces cerevisae*), which have integrated in their genome the genes of the human AHR (hAHR) and the human AHR nuclear translocator as well as a reporter gene cassette. This recombinant yeast strain was originally described by Miller (1999). Fox et al. (2008) describes the theoretical background of recombinant yeast based nuclear receptor-signalling reporter assays and the general protocol.

The procedures of the YDS are illustrated in Figure 4. The binding of a pollutant to the AHR activates the expression of a 'reporter' in the yeast cells which is the β-galactosidase. To visualise this enzyme release, the enzyme substrate chlorophenol red-β-D-galactopyranoside (CRPG) is added and converted to the orange chlorophenol red, which can be measured and quantified photometrically.

Figure 4: Schematic workflow of the Yeast Dioxin Screen (YDS)



The method follows the principles of ISO 19040-1:2018, using a different yeast strain. OD means optical density.
Source: BfG (2022). Edita Aksamitiene (2009) has the copyright of the images of the 96-well plates.

The YDS uses β-naphthoflavone as a reference compound to derive biological equivalence concentrations to translate the measured biological effect, in this case the AHR-binding, to the concentration of a reference compounds (see ISO 23196:2022). Binding and activation of the AHR in the YDS by unknown compounds is basically correlated with the strong binding of β-naphthoflavone to obtain a measure of the effect potency. β-Naphthoflavone belongs to the PAH and is a known, strong agonist of the AHR.

The water samples were used in the YDS as 1000-fold concentrated extracts. The extracts were diluted with the yeast medium and analysed at two dilution levels. The appropriate final dilutions were determined in a preliminary test and then applied to all samples. The final concentration factor is considered in the calculation of the biological equivalence concentration.

As an experiment, the water samples of S2 were examined also as native samples in the YDS in order to test whether hAHR activation can be detected also without enrichment of the samples. This was to demonstrate that WET testing in YDS would be possible in principle. The results of these tests are not presented in this report because it was only one exemplary test run. However, the results showed comparable activation potentials of the CL and the OL samples in the YDS. The samples were measured at three different conditions: 1) without filtration, containing all solids and particles, 2) supernatant after precipitation, and 3) after precipitation and filtration of supernatant. It was shown that the β-naphthoflavone equivalence concentrations (NF-eq) for the CL discharge sample decreased from over 40 µg/l in 1) to

<10 µg/l after filtration in 3). This suggests that AHR active compounds may have been particle bound and removed by precipitation and filtration. Overall, the findings demonstrated that WET testing of scrubber effluents for dioxin-like effects in YDS may potentially be possible. However, the influence of unfavourable sample properties such as low pH, high salinity, turbidity and suspended solids on the YDS would have to be systematically investigated at first. An influence of the salinity on the growth of the yeast cells was for instance only seen >20 PSU.

2.4.2.2 Ames test

Ames (*Salmonella*) fluctuation test followed ISO 11350:2012. The test can be described as a bacterial reverse mutation test and is usually employed to detect genotoxic activity in aqueous environmental samples. It detects mutation-inducing agents as they revert mutations present in genome of the bacteria and restore the functional capability to synthesize the essential amino acid histidine. Several *Salmonella typhimurium* strains with mutations in the histidine (his) operon are available and the mutation they detect is either a point mutation (base pair substitution) or a frameshift mutation (addition or deletion of one or more base pairs). Some strains have been further genetically modified which distinguishes them by several specific features like enhanced sensitivity or substance specificity.

The Ames tests were conducted using four different strains, of which TA98 and TA100 were applied at the laboratory of the BfG, and YG1041 and YG1042 at the UBA-laboratory. TA98 and TA100 can be described as the 'parent' strains which have few genetic modifications besides a base pair substitution (TA100) and a frameshift mutation (TA98) in the *his* operon. The test strains YG1041 and YG1042 additionally show enhanced *o*-acetyltransferase and nitroreductase activity. These strains cannot only detect the mutagenic mechanism, like TA98 and TA100, but also activate pro-mutagenic aromatic amines and nitro aromatic compounds (Hagiwara et al., 1993).

Bacteria and other cell-based *in-vitro* assays usually require the addition of metabolic enzymes which they lack, in order to mimic the *in-vivo* metabolic situation in vertebrates. Most commonly exogenous metabolic activity is introduced by the addition of rat liver S9 enzyme fraction. Hence, the Ames fluctuation test is preferably performed without as well as with exogenous metabolic activation by S9 addition, to also detect substances which require metabolic activation to become mutagens (so called pro-mutagens).

Briefly, the Ames tests were started with an overnight *S. typhimurium* culture of a defined cell-density which was exposed to one or various dilutions of the extracted water samples for 100 min at 37 ± 1°C in 24-well plates. After exposure, a new medium containing the pH indicator dye bromocresol purple was added to the bacteria. Subsequently, the different treatment and control batches are transferred from the 24 to 384-well plates, thus one well was distributed to 48 wells, and incubated for 48 h. The negative control treatment was the culture medium containing the solvent of the extracts, DMSO, and the positive control substances were 4-nitro-*o*-phenylenediamine (for TA98 without S9), nitrofurantoin (for TA100, YG1041 and YG1042, all without S9), and 2-aminoanthracene (for all four strains with S9). Mutagenic activity of the test sample was determined by counting the number of yellow (positive) wells of each treatment, where the purple colour had shifted to yellow due to the regained metabolism of 'revertant' bacteria. The lowest dilution of the test samples, which did not show mutagenic effects (i.e. revertant yellow wells) above the control level, i.e. the LID, defined the mutagenic potential of the samples. The higher the LID, the higher the mutagenic activity of the sample. For the *S. typhimurium* strains YG1041 and YG1042 only one dilution was measured, and the mutagenic activity of a sample was defined by the number of revertant wells in comparison to the negative control condition.

2.4.3 Fish-egg test

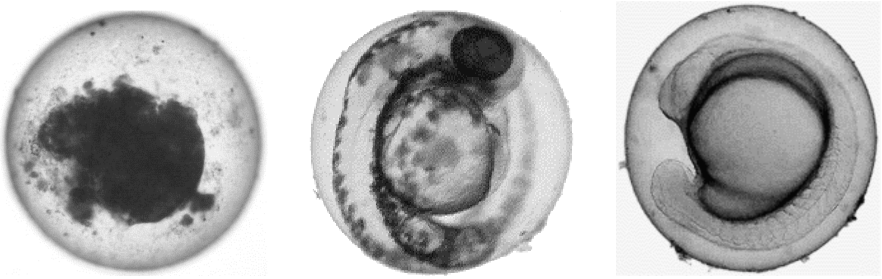
The fish-egg test with the eggs of zebrafish (*Danio rerio*) is designed to determine the acute toxicity of wastewater constituents and wastewater on embryonic stages of fish. It was established as an alternative test to the acute fish toxicity test (ISO 7346-1, ISO 7346-2 or OECD 203) and is considered to be a 'non-animal' test, since the central nervous system of the embryos is considered as not yet fully developed during the test period.

The fish-egg test was performed according to DIN EN ISO 15088 in 24-well plates at 26 ± 1°C, with 10 eggs per treatment. Freshly fertilised zebrafish eggs have been exposed to diluted extracts (final concentration factor for ship S1 = 1 for ship S2 to S4 = 2) and control conditions for a period of 48 h. The negative control condition was standard dilution water according to ISO 7346-1 and ISO 7346-2, the positive control substance was 3.7 mg/l of 3,4-dichloroaniline. After 24 h and 48 h, three apical observations, as shown in Figure 5, were recorded as indicators of lethality:

- coagulation of fertilised eggs,
- lack of heartbeat,
- lack of detachment of the tail-bud from the yolk sac.

At the end of the exposure period, acute toxicity is determined based on the three apical observations recorded in each treatment. The lowest dilution at which 90 % of the fertilised eggs did not show any of the three lethal endpoints, defined the LID of the test.

Figure 5: Apical observations on the fish-egg test



Coagulation of fertilised eggs (left), lack of heartbeat in a 48h embryo (centre) and lack of detachment of tail-bud from the yolk sac in a 24h embryo (right). UNIFISH-group (Fraunhofer IME) has the copyright of the fish embryos images.

2.4.4 Statistical evaluation

The results of the WET and the YDS tests were subject to a statistical analysis to determine statistical differences between the samples of the different sampling points on each ship. Each sample type was also compared between the different ships but the results of this analysis are not depicted in the bar charts of the results section.

Statistically significant differences were determined by applying an ANOVA followed by a Tukey HSD post-hoc test ($p<0.001$) for a pairwise comparison. The statistical analysis was performed using the open source solution RStudio, an integrated development environment for the programming language R.

2.5 Sampling and analyses of fuel and lubricating oil

Fuel oil and lubricating oil used in the ship engines were sampled from all four ships and analysed for metals and 16 EPA PAH. The analyses were conducted by the laboratory of Bureau

Veritas and their results allowed to better identify the source of pollutants in the scrubber discharge water. Additionally, sulphur content was determined in fuel oil samples by the laboratory of BSH. As mentioned above, fuel oil sulphur content and sulphur concentration in water samples were used to estimate the CL-specific discharge flowrate. Table 8 lists the parameters and their analysis method on fuel and lubricating oil samples.

It was desired to conduct the samplings on ships burning fuel that is representative of the global market for ships operating with scrubbers. All sampled ships operated with heavy fuel oil (HFO) classified as RMG 380 (in accordance with ISO 8217) with sulphur content above 2 % (m/m) as stated in the bunker delivery notes.

The sampling points for the fuel oil were as close to the inlet of the ship engine as feasible and safely possible according to the SAP. This means that the sampling points for fuel oil were located downstream the treatment and conditioning systems. There were no special requirements for the lube oil sampling points. For ships 1-3, lube oil already in service was sampled from the cooling system; for ship 4, from the storage tank. Details about the sampling material and storage as well as methods for sample preparation and analyses are given in the SAP.

Table 8: Analysis methods for fuel and lubricating oil

Parameter	Analysis method
Metals [As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, Zn]	IP 501 - modified for determination of additional elements (ICP-OES)
[Hg]	UOP 938
16 EPA PAH	CMA/3/B [i.]
Sulphur [ii.]	EN ISO 8754 (XRF spectroscopy)

Abbreviations: 16 EPA PAH, Priority PAH listed by the US Environmental Protection Agency; As, Arsenic; Cd, Cadmium; Cr, Chromium; Cu, Copper; Fe, Iron; Hg, Mercury; ICP, Inductively coupled plasma; IP, Institute of Petroleum; Mn, Manganese; Ni, Nickel; OES, Optical emission spectrometry; Pb, Lead; Sb, Antimony; UOP, Universal Oil Products Company; V, Vanadium; XRF, X-ray fluorescence; Zn, Zinc.

i. CMA method was developed by the Flemish Institute for Technology Research and is comparable to EN 16143 (for extender oils) but has broader range of application.

ii. Sulphur content was only determined in fuel oil samples.

3 Results and discussion

The results of the chemical and ecotoxicological analyses on the scrubber water samples as well as on the composition of fuel and lube oil are presented and discussed in this section. Moreover, calculated emission factors and water treatment efficiencies as well as the evaluation of the online monitoring are included here. Only selected results are included in this report. Additional data related to sections 3.1 to 3.5 can be found in 'Supplement B: Results of chemical characterization'.

In sections 3.1 and 3.2 in this report:

- OL-inlet water stream refers to the inflow water in OL operation (OL/IN samples),
- OL-discharge water stream refers to outflow water from OL operation before dilution (OL/BD samples), and
- CL-discharge water stream refers to outflow water from the holding tank from CL operation prior to any dilution (CL/OU samples).

Sampling point OL/BD (and not OL/OU) is taken as OL-discharge as it allows to derive the pollutants enrichment. The dilution water is only used to increase the pH in the discharge water and in many cases the flowrate is not known accurately. Sampling point CL/OU (and not CL/AT, after treatment) is taken as CL-discharge as the storage in the holding tank might alter the water quality and this stream represents usually a whole CL operation (see section 2.2). Both OL-discharge and CL-discharge are considered relevant for the environmental assessment.

3.1 Chemical characterization of water samples

3.1.1 General parameters

The results of the general parameters in OL-inlet, OL-discharge and CL-discharge are presented in Table 9. The reported values for temperature, pH, salinity and turbidity derive from the measurements conducted on board right after sampling; the other values correspond to the results of the laboratory analyses. The compilation of all results can be found in Supplement B.

There was a clear temperature increase in the discharge water as a result of the contact with the hot exhaust gases (around 200 – 400 °C). In OL, the temperature increase was between 8 and 15 °C and showed a relation with the specific flowrate. In CL-discharge, the temperature difference compared to OL-inlet (representative of the receiving water) was between 4 and 18 °C. Here, the recirculated water might reach more elevated temperatures, but after treatment the bleed-off is usually stored prior to discharge where it cools down. In general, the elevated temperature of the discharge water is considered not to be of environmental concern due to the expected high dilution in the receiving waters (Hufnagl et al., 2005), but impacts on aquatic ecosystems cannot be excluded for smaller enclosed water bodies, where temporary water temperature rise could occur.

The pH of the seawater in the sampling regions usually fluctuates between 8.0 and 8.4 (see Supplement B), with lower variations in the North Sea. The pH values in the OL-inlet in S1 and S2 were slightly lower than the range given above as this is brackish water with lower salinity and alkalinity. All discharge water samples had a lower pH than the inlet water. The pH in OL-discharge, prior to the dilution (OL/BD), ranged from 3.0 to 4.9. The pH after dilution (OL/OU) was between 4.6 and 5.2. By comparing the pH results from the portable device, mobile cabinet and laboratory (see Supplement B), almost all delayed measurements of OL/BD and OL/OU were lower than the measurements *in situ*, in some cases with a difference of even more than one unit, which is very significant when considering that the pH-scale is logarithmic. That was not the case for the CL samples. It is assumed that in the OL samples the equilibrium of the carbonate system was not yet reached during the *in situ* measurements. In both water streams (OL/BD and OL/OU) the pH change is sudden. Upstream the sampling point OL/BD, the scrubbing process decreases the water pH due to the absorption of sulphur dioxide. Upstream the sampling point OL/OU, the scrubber discharge water is diluted with seawater, causing a pH increase.

The alkalinity in the OL-inlet samples (1.8 – 2.5 mmol/l) were typical for the sampled regions, namely the Baltic Sea and the North Sea. The alkalinity in the OL-discharge samples were below the limit of quantification (LOQ: 0.3 mmol/l). The CL-discharge alkalinity ranged from 2.8 to 8.0; here, an alkaline solution (sodium hydroxide) was added to the washwater to neutralize the generated acids, which caused these higher values as compared to OL discharges. The potential environmental effects of the acidic discharges from OL operation have been assessed by other studies (Dulière et al., 2020; Gadd et al., 2021; Teuchies et al., 2020). Higher effects have been found in harbors and their vicinities as well as in coastal areas with high shipping activity; there, the modelled pH decrease ranged from 0.015 to 0.120. Dulière et al. (2020) indicated that the effects of scrubber discharges on acidification of the local waters is equivalent to 10 to 50 years of acidification associated to the increase of carbon dioxide concentration in the atmosphere. In other areas, the effects were considered negligible (Gadd et al., 2021).

The salinities of the OL-inlet samples reflected the brackish (S1 and S2) and marine (S3 and S4) conditions of the sampling regions in the Baltic Sea and North Sea, respectively. The OL-discharge salinities were very close to the OL-inlet values. In contrast, CL-discharge salinities were significantly higher than OL-discharge values. This was due to the continuous recirculation of the washwater. By this, there was an enrichment of salts formed by sodium from the alkaline solution and by the absorbed sulphur in form of sulphate, sulphite and bisulphite, depending on the pH and the redox conditions (Lahtinen, 2016). Thus, there is a correlation between salinity and sulphur concentration in the CL-discharge. The enrichment of sulphur compounds in CL-discharge is also an indication of how ‘frequent’ the washwater is recirculated before being taken out of the system as bleed-off water. It is assumed that the sulphur removal during bleed-off treatment is negligible. Therefore, the sulphur concentrations could be used to calculate the specific flowrates in the CL-mode.

Turbidity and suspended solids are expected to have certain relations. There was a clear increase in water turbidity in the OL operation, except for S1 where the employed turbidity sensor had a higher limit of detection (LOD: 2 FNU). However, none of the turbidity differences between OL-inlet and OL-discharge reached 25 FNU (set as limit value in the ‘EGCS Guidelines’), and it is unlikely to happen during OL operation. Three of the CL-discharge samples exceeded 25 FNU considerably.

Table 9: Results of general parameters

Parameter [unit]	S1			S2			S3			S4		
	OL-inlet	OL-discharge	CL-discharge	OL-inlet	OL-discharge	CL-discharge	OL-inlet	OL-discharge	CL-discharge	OL-inlet	OL-discharge	CL-discharge
Temp. [°C]	9.6	17.7	19.0	3.3	18.3	7.1	19.1	27.5	34.0	19.4	27.7	37.2
pH [-]	7.3	4.9	6.5	7.6	3.0	5.6	8.1	3.0	6.4	8.2	4.6	7.1
Alkalinity [mmol/l]	1.8	<0.3	3.8	1.9	<0.3	2.8	2.5	<0.3	3.5	2.4	<0.3	8.0
Salinity [PSU]	8.7	9.2	14.2	7.8	8.0	11.0	34.6	33.4	53.8	33.2	32.7	57.9
Sulphur [mg/l]	230	280	1700	180	275	1480	857	928	15000	790	857	23700
Turbidity[i] [FNU]	5.5	5.7	13.3	2.4	8.7	127	1.1	4.8	264	0.63	11.6	46
Suspended solids [mg/l]	<2.0	3.0	5.6	5.6	5.8	16.0	9.2	13.0	73	<2.0	9.2	5.9

OL-inlet: OL/IN; OL-discharge: OL/BD; CL-discharge: CL/OU.

[i] In S1, turbidity was measured with the EGC Water Analyzer only; for S2-S4 the measurements were conducted additionally with the portable turbidimeter and the results are reported here.

3.1.2 Nitrogen compounds

Total nitrogen, nitrate, nitrite and ammonium were measured in the laboratory. The results for the inlet and discharge water are presented and compared to environmental concentrations in Table 10. Most of the concentrations in the OL-inlet are <LOQ; indeed, the environmental concentrations in the sampled regions range from <LOQ to LOQ. Likewise, many OL-discharge concentrations are <LOQ and it was not feasible to estimate an enrichment of nitrogen compounds. In CL-discharge the enrichment of nitrogen compounds was clear, however, there was no trend in the abundance of the nitrogen compounds: nitrate, nitrite and ammonium showed the highest concentrations in different samples. The equilibrium between nitrogen species is dominated by the redox conditions. The high concentration of ammonium in the CL-discharge of S4 might have been caused by residues of the flocculant polyacrylamide applied for the water treatment.

Table 10: Results of nitrogen compounds

Compound [mg N/l]	Environmental concentration	S1			S2			S3			S4		
		OL-inlet	OL-discharge	CL-discharge	OL-inlet	OL-discharge	CL-discharge	OL-inlet	OL-discharge	CL-discharge	OL-inlet	OL-discharge	CL-discharge
Total-N	0.3 - 0.4	<0.4	0.6	16	<0.9	1.0	19	<9.0	<9.0	100	<9.0	<9.0	220
NO_3^-	0.02 - 0.16	<0.2	<0.2	<0.2	<0.2	<0.2	8.0	<0.2	<0.2	70	<0.2	<0.2	16
NO_2^-	0.003 - 0.01	<0.01	<0.01	8.2	0.01	<0.01	<0.01	<0.01	0.12	25	<0.01	<0.01	9.1
NH_4^+	0.01- 0.04	<0.04	<0.04	0.23	<0.04	<0.04	0.06	<0.04	0.09	0.07	0.06	0.06	38

OL-inlet: OL/IN; OL-discharge: OL/BD; CL-discharge: CL/OU; Total-N: Total nitrogen.

As stated in Marin-Enriquez et al. (2021), the limit value for nitrate in the 'EGCS Guidelines' was set to mitigate the risk of eutrophication by preventing discharges with high concentrations of nitrate from nitrogen oxides (NOx)-removing scrubber systems. However, to our knowledge, there are no scrubber systems designed to remove NOx (besides SOx) on the market. The nitrate limit value (60 mg NO_3^-/l) was set based on the assumptions:

- 17 g/kWh as NOx emission factor in the exhaust gas,
- 12 % removal efficiency of NO_2 from the total NOx in the exhaust gas and
- 45 m^3/MWh as specific discharge water flowrate.

Linders et al. (2019) reported that most of the reviewed studies confirmed the limited capacity of scrubbers for NOx removal, keeping nitrate concentrations well below the limit value of the 'EGCS Guidelines'. The results from ImpEx are in line with the statement above, showing that all OL-discharge samples resulted in concentrations <LOQ (i.e. <0.89 mg NO_3^-/l or <0.20 mg NO_3-N/l). Indeed, the assumptions listed above may apply to rare cases and not to a typical scenario. Grigoriadis et al. (2021) reported mean NOx emission factors for ships per engine type and tier standards in the range of 1.0 – 14.4 g/kWh. The document MEPC 55/4/5 (United Kingdom, 2006) states that scrubbers may reduce NOx by 2 to 5 % at most; while Winnes et al. (2018) reported a NOx removal by scrubbing of ~1 %.

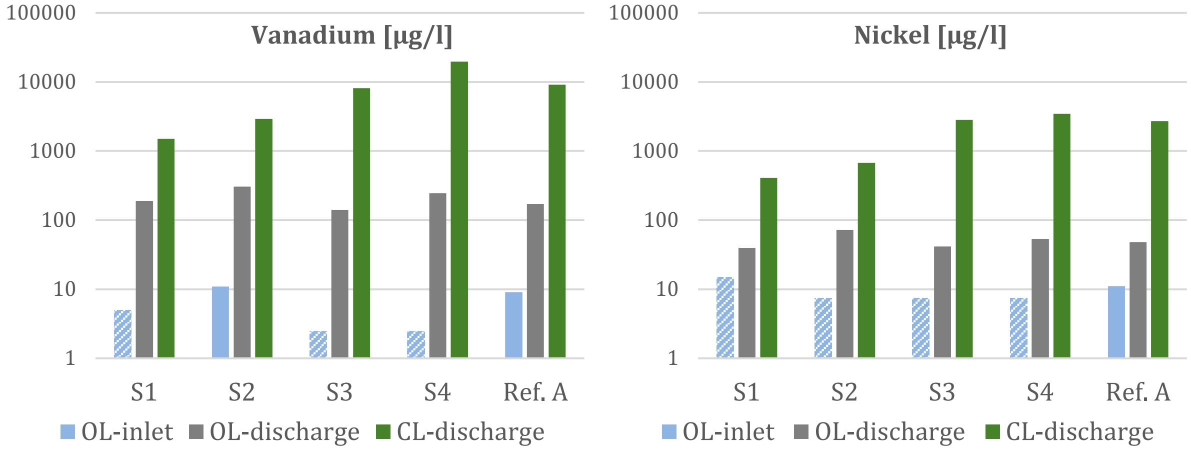
Although many of the laboratory results for nitrate compounds resulted <LOQ, total nitrogen emission factors were calculated for the CL-discharge and they ranged from 35 to 66 g/MWh. Assuming the mean NOx emission factor for medium speed diesel engines from Grigoriadis et al. (2021) for the sampled ships within ImpEx, the NO_2/NOx removal rates result between 1.4 % and 2.1 %. Thus, our results confirm the limited capacity of scrubbers for removing NOx and, as a consequence, relatively low concentrations in the discharge water.

Considering those findings and the already in force NOx regulations within MARPOL Annex VI as well as the fact that part of the exhaust NOx emissions would end up in the sea regardless of the use of scrubbers, we conclude that nitrates should not be a matter of concern in scrubber discharges. Similarly, Linders et al. (2019) and the US EPA (2011) concluded that the potential for significant increase of primary production and eutrophication as a consequence of scrubber discharges appears to be low. For the CL-discharges, however, where the total nitrogen reached maximum concentration of 220 mg/l and discharges typically occur irregularly and at specific points like in the proximity of areas with a discharge ban, this conclusion might be taken cautiously.

3.1.3 Metals

The complete laboratory results of the metals determination are found in Supplement B. Figure 6 presents the results of vanadium and nickel in OL-inlet, OL-discharge and CL-discharge as obtained from the analyses by HU. Vanadium and nickel are indicated by other studies as the metals with the most relevant concentration in scrubber discharge water as compiled by Marin-Enriquez et al. (2021), moreover, there is a clear relation with the fuel oil composition (see section 3.5). Figure 6 includes as 'Ref. A' average concentrations reported by Hermansson et al. (2021) based on the review of several studies. A logarithmic scale for a better comparison of all results was used. Both, vanadium and nickel results of OL-discharges, are close to the reference average values. The present results show significant higher concentrations in CL-discharge (V: 1500 – 19700 µg/l; Ni: 410 – 3470 µg/l), on average about 40 times greater than the OL-discharge (V: 140 – 308 µg/l; Ni: 40 – 73 µg/l) concentrations for vanadium and nickel. Teuchies et al. (2020) also found concentrations of metals on average 40 times higher in CL-discharge than in OL-discharge.

Figure 6: Vanadium and nickel concentration in discharge water



Striped bars indicate that the result was below the limit of quantification (LOQ). In that case, the assigned value is LOQ/2. A logarithmic scale is used in both diagrams.
Ref. A: Hermansson et al. (2021)

For other metals, many results were <LOQ and are not as consistent as for vanadium and nickel. Here, it is important to also consider other pollution sources, which may be more relevant than the fuel oil like corrosion of ship's and scrubber system's materials including the sampling point itself. For the assessment of those metals in terms of an enrichment in the discharge water, additional laboratory results with lower LOQ from HEREON for the determination of metals (in dissolved form) for selected water samples were considered as well. The analysis results are found in Supplement B. It should be noted that the analysis of HEREON did not include arsenic, chromium, antimony and mercury. The environmental (background) concentrations of the sampled regions were also considered to identify potential pollutants enrichment even in the inlet water. The data was extracted from the marine environment databank MUDAB, version 1.5.2 (https://geoportal.bafg.de/MUDABAnwendung/) and is presented in Figure 13 and Supplement B. The calculated emission factors of the water samples and the fuel oil also served as reference for the assessment. No statistical analyses were conducted due to the low amount of data (only from four sampled ships). Table 11 summarizes the results of the assessment

considering the above-mentioned information. The indicated potential enrichment for every metal could serve as guidance for the environmental risk assessment of discharge water, but it should not be decisive because of the different environmental profiles (e.g. persistence, bioaccumulation potential and toxicity) of every compound and their background concentration in the region of interest.

The classification of the potential enrichment used in Table 11 was determined on own criteria based on the observed emission factors with consideration (subtraction) of the average environmental concentrations. Thus, emission factors <1 mg/MWh were considered extremely low, <100 mg/MWh low, <1000 mg/MWh high and >1000 mg/MWh very high.

From this assessment, the potential enrichment of cadmium and mercury was determined to be extremely low. In addition, they were <LOQ in the fuel and lube oil (<1 mg/kg for cadmium and <1 µg/kg for mercury) and their concentration in discharge water are in the same range as the average environmental concentrations. Therefore, their presence in discharge water might be exclusively related to the environmental concentration. This differs from other studies that assigned relatively higher emission factors for these compounds (Hermansson et al., 2021; RVIM, 2021).

To our knowledge, the analysis of rare-earth elements, such as cerium, lanthanum and yttrium, in scrubber discharge water is a novelty of this study. The evaluation of the results concludes that there is an enrichment in the discharge water with estimated emission factors <10 mg/MWh. This confirms the statement made by Gadd (2020), indicating the possible presence of rare-earths in scrubber discharge water because these elements are contained in fuel oil. The environmental impact of rare-earth elements is a novel research field that has gained more attention in recent years due to the higher application of these compounds in different products such as electronics and their potential occurrence in the environment as a result of increased production and use (Piarulli et al., 2021).

Other metals such as cobalt, gallium, indium, titanium and zirconium showed as well elevated concentrations in OL-discharge compared to OL-inlet (see Supplement B).

Table 11: Potential enrichment of metals in discharge water

Compound	Potential enrichment [i.]	Justification	Possible source of pollution
As	Low	OL-discharge concentrations are close to environmental concentrations. CL samples show higher concentrations.	Unclear, probably fuel oil (as concentrations are higher in CL samples) and corrosion of scrubber steel components.
Cd	Extremely low	Environmental concentrations, in OL-inlet and in OL-discharge are in the same range. Concentrations in fuel oil and CL samples are <LOQ.	-
Cr	Low	All OL samples are <LOQ. Some CL samples are clearly higher than environmental concentrations.	Probably corrosion of metal components of scrubber and fuel oil (as concentrations are higher in CL samples).
Cu	Very high	Elevated concentrations in most water samples (including OL-inlet) compared to environmental concentrations.	Ship’s antifouling system, cathodic pipe protection and corrosion of metal components of the scrubber system.

Compound	Potential enrichment [i.]	Justification	Possible source of pollution
Fe	Very high	High concentration and emission factors in discharge water samples and fuel oil. In S3, emission factors of discharge water exceed the ones from fuel oil.	Fuel oil and corrosion of metal components of scrubber system.
Hg	Extremely low	Most of the samples were <LOQ. Environmental concentrations, OL-inlet, OL-discharge and CL-discharge are in the same range. Concentration in fuel oil is <LOQ.	-
Mn	High	Elevated concentrations in OL- and CL-discharge water.	Unclear, probably from corrosion of metal components of scrubber system.
Ni	Very high	High concentration and emission factors in discharge water samples and fuel oil have a clear relation.	Fuel oil and, to a lesser extent, corrosion of metal components of scrubber system.
Pb	Low	Slightly elevated concentrations in OL-discharge and clearly higher concentrations in some CL samples.	Unclear, probably fuel oil and corrosion of metal components of scrubber system.
Sb	Very low	There is no environmental concentration data. All water samples concentrations are <LOQ, except for the CL samples of S3 that show very low emission factors. Concentration in fuel oil is <LOQ.	-
V	Very high	High concentration and emission factors in water samples and fuel oil have a clear relation.	Fuel oil.
Zn	High	Elevated concentrations in most water samples compared to environmental concentrations.	Ship's corrosion protection system, corrosion of metal components of scrubber system, fuel and lube oil.
Rare-earth elements (e.g. Ce, La, Y)	Low	There are no environmental concentration data. OL-discharge concentrations (in ng-range) are clearly higher than the OL-inlet concentrations.	Probably fuel oil.

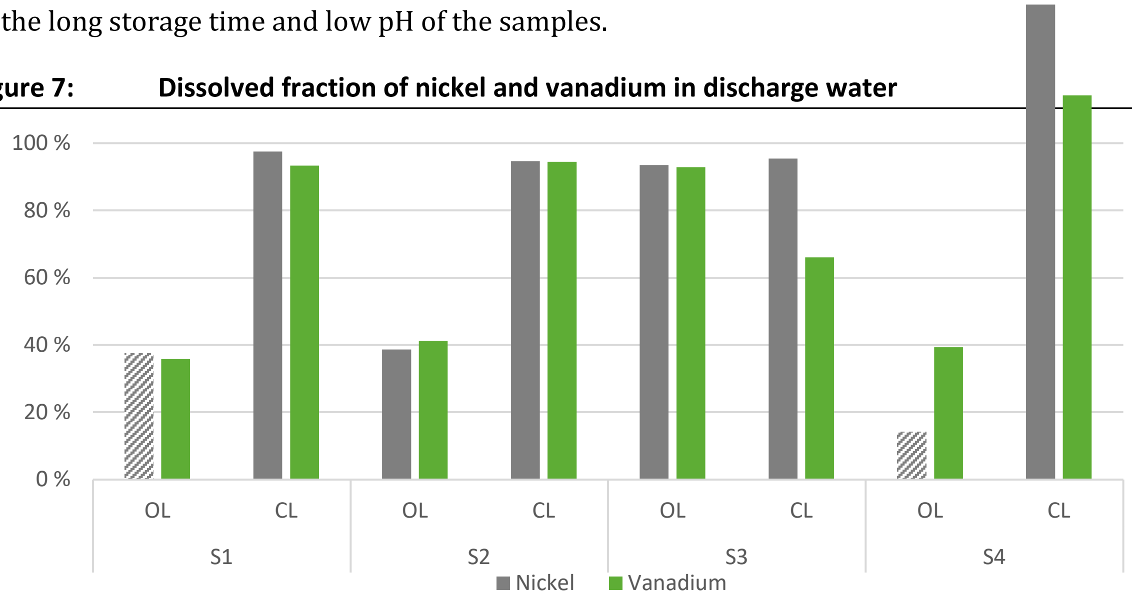
Abbreviations: As, arsenic; Ce, cerium; Cd, cadmium; Cr, chromium; Fe, iron; Hg, mercury; La, lanthanum; LOQ, limit of quantification; Mn, manganese; Ni, nickel; Pb, lead; Sb, antimony; V, vanadium; Y, yttrium; Zn, zinc.

i. The classification of the potential enrichment was determined on own criteria based on the observed emission factors with consideration (subtraction) of the average environmental concentrations. Emission factors <1 mg/MWh were considered extremely low, <100 mg/MWh low, <1000 mg/MWh high and >1000 mg/MWh very high.

Metals were determined in untreated and filtered (0.45 µm) samples in order to obtain total and dissolved concentrations, respectively. The dissolved fractions of the water samples were calculated and assessed. Again, nickel and vanadium showed the most consistent results. These are presented in Figure 7 for the discharge samples. It is observed that the dissolved fraction of nickel and vanadium in OL-discharge is close to 40 % and in CL-discharge above 90 %. A deviation is observed for S3 in OL-discharge. It should be noted that during sampling 3, there was a delay in the delivery of the samples to the laboratories due to a ship schedule modification. The longer storage time of the samples might have caused a change in the equilibrium between dissolved and particulate species.

It should be stressed that the results referred in Figure 7 are from the measurements of HU laboratory and differed from the results of HEREON laboratory, which only conducted analyses of certain samples in the dissolved fraction. The differences between the results of both laboratories are considered acceptable and were not deeply evaluated as the measurements followed different analysis methods and, as mentioned above, the samples delivered to HEREON were stored for a long time at room temperature and without conditioning. Generally, the concentrations in OL-discharge reported by HEREON (in dissolved form) were higher than the concentrations reported by HU (in dissolved form); indeed, the results from HEREON (in dissolved form) were close to the total concentrations reported by HU. These observations could be explained also by a change in the equilibrium between dissolved and particulate species due to the long storage time and low pH of the samples.

Figure 7: Dissolved fraction of nickel and vanadium in discharge water



Striped bars indicate that the concentration of the metal in dissolved form is below the limit of quantification (LOQ). In that case, the assigned value is LOQ/2.

3.1.4 Oil content and 16 EPA PAH

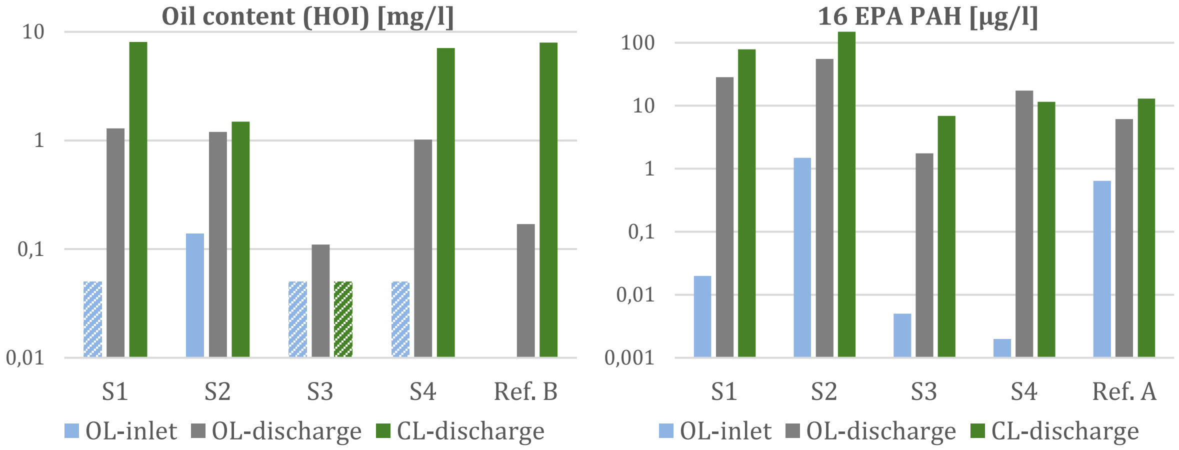
The full laboratory results of oil content and PAH determination by HU are found in Supplement B. Figure 8 presents the results in OL-inlet, OL-discharge and CL-discharge. It includes as reference average concentrations reported in the literature.

The hydrocarbon oil index (HOI) was determined as indicator of the oil content. Oil content in OL-inlet samples was <LOQ (0.1 mg/l), except for S2 (0.14 mg/l). There are no environmental data available for comparison, however, presence of oil should not be expected in the inlet samples. The presence of oil residues in OL-inlet in S2 as well as the elevated concentrations of other compounds such as 16 EPA PAH, vanadium and nickel are an indication of a pronounced contamination of the inlet water in S2. The oil content in OL-discharge was in the range 0.1 – 1.3 mg/l; three out of the four samples exceeded slightly 1 mg/l. There is no discharge limit for oil content in scrubber discharge water, however, 1 mg/l served as reference to define the discharge limit in the 'EGCS Guidelines' for PAH as surrogate parameter (Marin-Enriquez et al.,

2021). CL-discharge showed oil concentrations between <0.1 and 8.1 mg/l and on average 4.6 times greater than in OL-discharge.

The concentrations of the 16 EPA PAH in OL-inlet samples were mostly <LOQ, as expected, based on the environmental concentrations. Only S2 showed significant elevated concentrations (see paragraph above). The sum of the 16 EPA PAH in OL-discharge was in the range of 1.7 – 55.6 µg/l, while in CL-discharge between 6.9 and 150 µg/l. The results show higher concentrations in CL-discharge, which were on average 2.4 times greater than the OL-discharge. It should be noted that the discharge concentrations in S1 and S2 are much higher than in S3, S4 and the average values from the literature. No issues from the sampling and analysis procedures were found that could explain those elevated values. In order to explain the high concentrations commented above, there are three factors that can affect the PAH concentration in the scrubber water: the fuel oil composition, the removal rate by the scrubbing process (transfer of PAH from the exhaust gas to the washwater) and the combustion efficiency. The concentration of PAH in the fuel used by S1 and S2 are close to the average concentration found in the literature (see Table 14). The removal rate of hydrocarbons by the scrubbing process in ships S1 and S2 is unknown; but the removal rate of particulate matter in the exhaust gas might not vary largely between the scrubber systems. It is assumed that the combustion efficiency is the main factor explaining the high concentrations of PAH. Ships S1 and S2 are relatively old and reported a high SFOC (see Table 3). Inadequate maintenance to the engine system could lead to a poor combustion causing elevated concentrations of unburnt oil residues including PAH in the exhaust gas. Another factor influencing the combustion efficiency is the suitability of the scrubber for the engine, as for ships S1 and S2 they were retrofits. A mismatch can lead to increased backpressure and older turbochargers may react more sensitive to an increase in exhaust backpressure. Further, a lower air-fuel ratio as measure to decrease NOx emissions could lead as well to a reduced combustion efficiency (incomplete combustion). It should be noted that also the results of the CL-discharge offer an evidence for the atypical high concentrations found in the OL-discharge of S1 and S2, which were not exceptional but are typical for the operation on board those ships.

Figure 8: Oil content (HOI) and 16 EPA PAH concentration in discharge water



Striped bars indicate that the result was below the limit of quantification (LOQ). In that case, the assigned value is LOQ/2. A logarithmic scale is used in both diagrams. Ref. A: Hermansson et al. (2021). Ref. B: Schmolke et al. (2020).

PAH were determined in untreated and filtered (0.45 µm) samples in order to obtain total and dissolved concentrations, respectively. The dissolved fraction for the water samples were calculated and analyzed. These are presented in Figure 9 for the discharge samples. The average dissolved fraction of 16 EPA PAH in OL-discharge was 72 % and in CL-discharge 25 %; it means PAH in dissolved form dominated in OL-discharge, while PAH in particulate form dominated in CL-discharge. Indeed, by assessing the mass fraction of the different PAH species, differences between OL- and CL-discharge can be observed (see Figure 10). The fraction of high-molecular weight PAH is higher and of naphthalene is lower in CL-discharge, when compared to the PAH distribution in OL-discharge. This could be caused by the intensive water recirculation and higher water temperatures in CL operation that could lead to volatilization of low-molecular weight PAH. The most abundant PAH species were phenanthrene, naphthalene and fluorene.

Figure 9: Dissolved fraction of 16 EPA PAH in discharge water

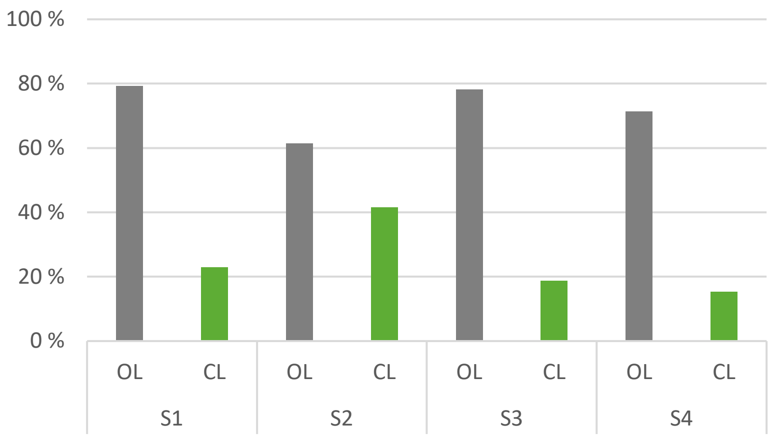
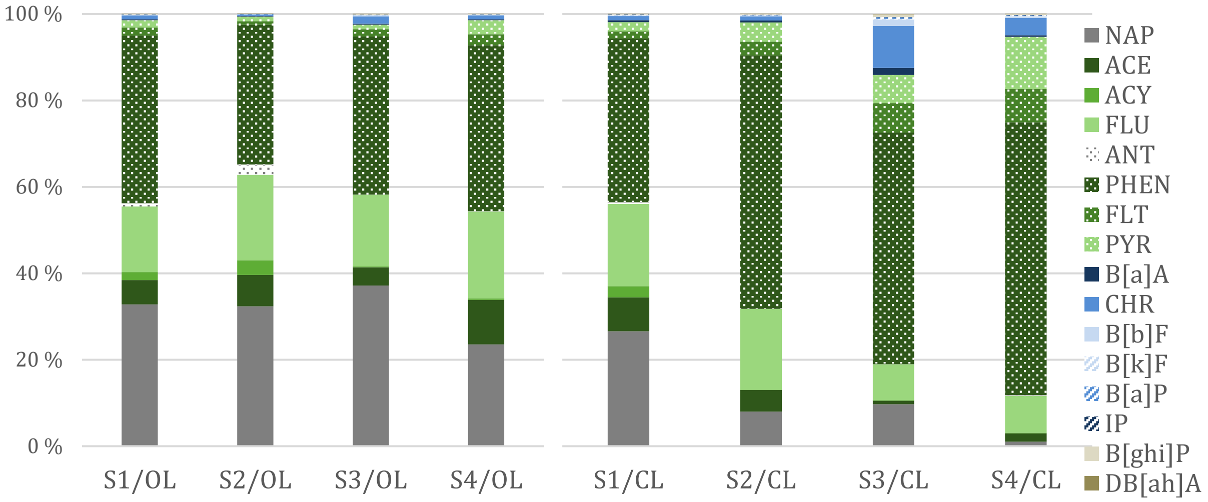


Figure 10: 16 EPA PAH distribution in discharge water

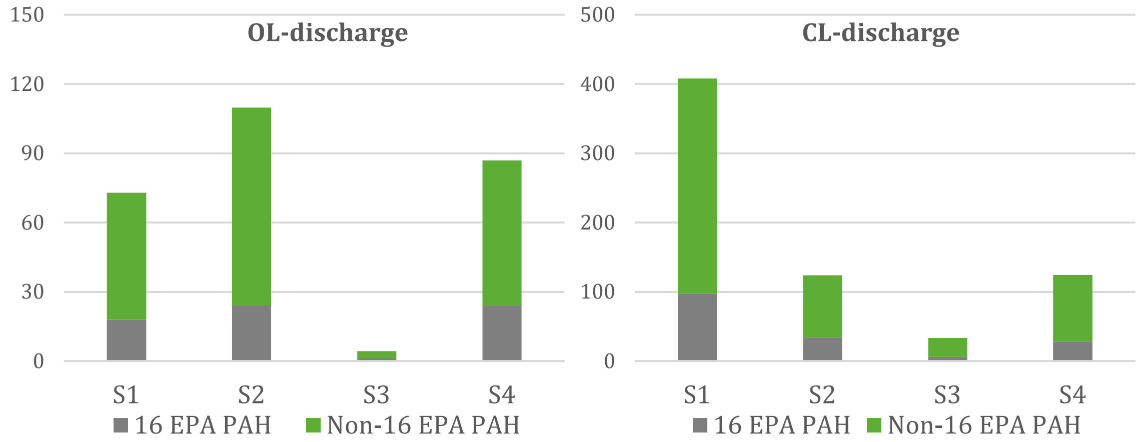


Abbreviations: ACE, acenaphthene; ACY, acenaphthylene; ANT, anthracene; B[a]A, benzo[*a*]anthracene; B[a]P, benzo[*a*]pyrene; B[b]F, benzo[*b*]fluoranthene; B[k]F, benzo[*k*]fluoranthene; B[ghi]P, benzo[*ghi*]perylene; CHR, chrysene; DB[ah]A, dibenzo[*a,h*]anthracene; FLT, fluoranthene; FLU, fluorene; IP, indeno[1,2,3-*cd*]pyrene; NAP, naphthalene; PHEN, phenanthrene; PYR, pyrene.

3.1.5 Extended list of PAH

The complete results of the extended list of PAH is found in Supplement B. As mentioned in section 2.3.2, the extended list of PAH considered within ImpEx and measured by WWU included about 70 compounds (including the 16 EPA PAH) in dissolved and particulate phase. The sum of the total concentration (including PAH in particulate and dissolved form) of the extended list of PAH is displayed in Figure 11, which shows the fractions covered by the 16 EPA PAH and the rest of the measured PAH (non-16 EPA PAH). The total concentration of the extended list of PAH was on average around four times higher than the sum of 16 EPA PAH in OL and CL discharge water. It should be stressed that the results of the 16 EPA PAH referred in this section are from the measurements of WWU laboratory, which differed slightly from the results of HU laboratory (reported in previous section). The differences between the results of both laboratories are considered acceptable and were not deeply evaluated as the measurements aimed different purposes and followed different analysis methods. Further, comparison of dissolved and particulate PAH concentrations should be done with care, because complete homogeneity during sample preparation can not be be guarranteed. Also, the concentrations in particulate phase were originally reported in µg/mg of dry mass and converted to µg/l by considering the solids concentration obtained from the centrifugation process, in order to obtain the total PAH concentration of the samples.

Figure 11: Total concentrations (in µg/l) of the sum of all measured PAH (16 EPA and non-16 EPA) in scrubber discharge water



As measured by WWU. The fraction of non-16 EPA PAH refers to the sum of the extended list of PAH excluding the 16 priority PAH by the US Environmental Protection Agency (EPA).

Andersson and Achten (2015) mentioned that there are PAH of considerably higher toxicity than that of the 16 EPA PAH. Therefore, it was decided to analyse the extended list of PAH including also alkylated PAH beyond the typical 16 EPA PAH. There might be more unknown PAH, like nitro-, oxy- and amino-PAH, which were not measured in this project.

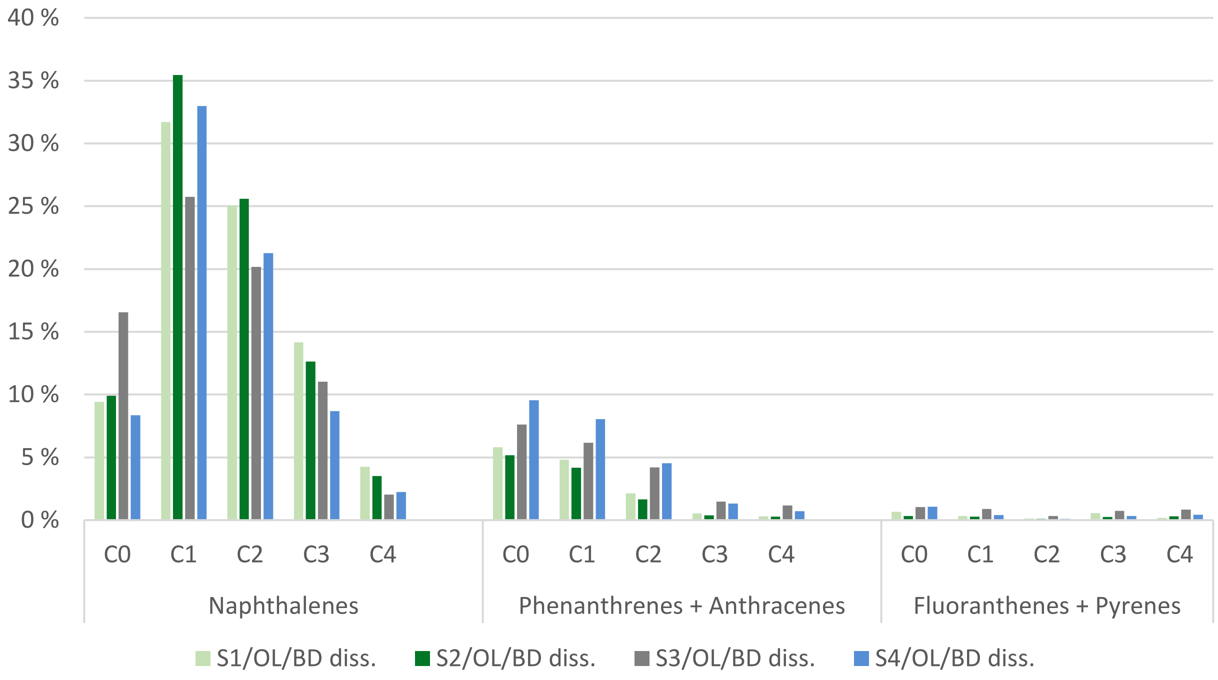
The alkylated PAH dominated the total PAH concentrations and, as expected in the dissolved fractions, were mainly low-molecular weight PAH (Figure 12). Figure 12 shows that the methyl (C1: 26 – 35 %) and dimethyl (C2: 20 – 26 %) naphthalenes were the most abundant alkylated PAH in dissolved form in OL discharge water, which together made-up around half of all PAH, while the parent naphthalene (C0) represented only 8 – 10 % with a spike of 17 % at S3. In absolute concentrations the parent naphthalene was on average 5 µg/l, however with a wide range from 0.34 – 9.6 µg/l in the OL dissolved samples before dilution and 0.09 – 12.6 µg/l in the CL dissolved outlet samples. The dissolved methyl (C1) naphthalene was detected from 0.5 – 44 µg/l in the OL outlet samples before dilution and 0.12 – 36 µg/l in CL outlet samples. The dimethyl (C2) and trimethyl (C3) naphthalenes occurred on average in 8 and 3 µg/l, respectively in both, OL and CL samples. The lowest PAH concentrations were generally found in S3.

The second largest group of alkylated PAH is represented by the phenanthrenes together with anthracenes. These two PAH have the same mass, therefore the peaks in the chromatograms are integrated together, same as fluoranthenes and pyrenes. Here the parent compound occurred in slightly higher concentrations (5 – 10 % of all PAH) than the mono-alkylated phenanthrene (4 – 8 %) with a continuously decreasing trend towards the tetramethyl (C4) phenanthrene. The concentrations of the dissolved parent phenanthrene/anthracene ranged from 0.26 – 8.8 µg/l on the OL discharge samples before dilution and from 0.36 – 18.0 µg/l in the CL samples. The particulate phenanthrenes/anthracenes ranged from 0.21 – 154 µg/l for the mono methyl (C1) phenanthrene/anthracene, with the lowest concentration in S2.

In Figure 12 the relative distribution of the C0-C4-naphthalenes shows a bell-shape pattern for the naphthalenes. According to Neff et al. (2004), Hindersmann et al. (2020) and Ghetu et al. (2021) a bell-shape distribution of the alkylated PAH indicates that the PAH have a petrogenic origin. For the phenanthrenes, no bell-shape distribution of the alkylated compounds could be observed. They show a decreasing abundance from the parent phenanthrene and anthracene (C0) down to C4, which indicates a rather pyrogenic origin according to Andersson and Achten (2015). Consequently, there is a mixed source of the alkylated PAH, i.e. a combination of rather petrogenic naphthalenes (high abundance in petrogenic PAH sources) and rather pyrogenic higher molecular PAH (high abundance in pyrogenic PAH sources). This finding is confirmed by the analysis of the PAH alkylation index, which is calculated by the sum of the parent PAH divided by the sum of parent PAH plus the C2-alkylated PAH, i.e. $\Sigma C0/(\Sigma C0+\Sigma C2)$, according to Hindersmann et al., 2020. The alkylation-index from the results in this study ranged from 0.36 to 0.50, which indicates the mixed source of the PAH with a tendency to more petrogenic PAH in the dissolved OL-discharge samples.

The results of this study also agreed well with the findings of Du et al. (2022). The authors indicated that the exclusive measurement of the 16 EPA PAH underestimated the total PAH concentration (including alkylated PAH) by a factor of 5.4 and that alkylated derivatives of naphthalene, phenanthrene and fluorene clearly dominated over the analysed PAH in scrubber discharge water. They also concluded that PAH found in scrubber discharge water are mainly of petrogenic origin, possibly with a pyrogenic contribution.

Figure 12: **Relative distribution of dissolved parent and alkylated PAH in OL scrubber discharge water**



Where 100 % is the sum of all depicted dissolved PAH per sample.

To relate the toxicity of the individual alkylated PAH, they are compared to the toxicity of benzo[*a*]pyrene, as it is commonly done. The toxicity of the single compounds then gets a toxic equivalency factor (TEF) in relation to benzo[*a*]pyrene, which is per definition 1. It should be noted that the toxicity data in the literature for PAH other than the 16 EPA PAH are very scarce, so that only certain compounds identified in the samples with relevant concentrations are evaluated.

Table 12 presents the toxicity (expressed in TEF) of some non-EPA PAH compounds. Dibenzo[*a,e*]pyrene and dibenzo[*a,l*]pyrene were detected in traces (up to 0.63 and up to 0.009 µg/l, respectively) in the particulate fractions of the discharge samples, while dibenzo[*a,i*]pyrene and dibenzo[*a,h*]pyrene were not found (<LOD). 7H-benzo[*c*]fluorene has been identified in almost all discharge samples with concentrations of up to 4.42 µg/l. With a TEF of 20, this compound significantly contributes to the total toxicity of the discharge water. 5-Methylchrysene and 1-methylpyrene have been identified in the particulate phase of all CL-discharge samples with total concentrations of 0.02 – 1.41 µg/l and 0.03 – 0.67 µg/l, respectively. 2-Methylnaphthalene was found in relevant total concentrations (0.25 – 44 µg/l) in all discharge samples. All these compounds contribute to the overall toxicity of the samples.

Table 12: Toxicity of PAH other than the 16 EPA PAH expressed in TEF

Compound	Toxicity (in TEF)	Reference
2-Methylnaphthalene	0.001	Moradi et al., 2022
1-Methylpyrene	0.1	Andersson and Achten, 2015
5-Methylchrysene	1	Richter-Brockmann and Achten, 2018
Dibenzo[*a,e*]pyrene	1	Richter-Brockmann and Achten, 2018
Dibenzo[*a,l*]pyrene	10	Richter-Brockmann and Achten, 2018
Dibenzo[*a,i*]pyrene	10	Richter-Brockmann and Achten, 2018
Dibenzo[*a,h*]pyrene	10	Richter-Brockmann and Achten, 2018
7H-benzo[*c*]fluorene	20	Richter-Brockmann and Achten, 2018

TEF is a toxic equivalency factor in relation to benzo[*a*]pyrene, which is per definition 1.

Sulphur-containing polyaromatic compounds were also determined. Dibenzothiophene (0.7 - 1.7 µg/l in OL-discharge and 1.2 - 8.8 µg/l in CL-discharge), 4-methyldibenzo[b,d]thiophene (0.3 - 1.5 µg/l in OL-discharge and 1.7 - 12.4 µg/l in CL-discharge) and 2,3-dimehtyldibenzo[b,d]thiophene (0.1 - 0.9 µg/l in OL-discharge and 0.5 - 7.9 µg/l in CL-discharge) were found in almost all discharge samples and covered up to 13% of the sum of all PAH analysed. Alkylated dibenzothiophenes are commonly found in residual fuels (Uhler et al., 2016) so they have a petrogenic origin. However, no information has been found for the specific environmental toxicities of the dibenzothiophenes and their derivatives.

3.1.6 Other organic pollutants

Benzene, toluene, ethylbenzene and xylene (BTEX), highly volatile halogenated hydrocarbons (HVHH), polychlorobiphenyls (PCB) and dioxins were measured in selected water streams. The complete results can be found in Supplement B.

No BTEX (<0.10 µg/l) were found in the OL-inlet, except for ethylbenzene (0.11 µg/l) in S1. The sum of BTEX in discharge water was in the range 0.3 – 2.8 µg/l in OL and 1.7 – 46.1 µg/l in CL, showing benzene the highest abundance. HVHH (<0.20 µg/l) were not found in any sample, except for dichloromethane (0.7 µg/l) in CL-discharge in S3.

PCB (<0.050 ng/l) and dioxins (<0.056 ng/l I-TEQ[4]) were not found in any water sample. However, analyses of CL sludge sampled during the same measuring campaign showed dioxins concentrations in dry matter from 28 to 87 ng/kg I-TEQ (equivalent to 0.5 – 2.9 ng/l I-TEQ). Please refer to Appendix B. Kjølholt et al. (2012) reported 26 ng/kg I-TEQ in CL sludge. It should be noted that hydrocarbons with higher molecular weight (with abundance in particulate form) are easily removed during CL water treatment (see section 3.3); thus, enriched in the sludge.

The non-target screening, a qualitative analysis, did not deliver information about further unknown pollutants, as the clear identification of single compounds from the GC-MS scans was not possible.

3.1.7 Background concentrations and inlet water

Environmental (background) concentrations of selected parameters in the sampled regions are included in Supplement B. The data were obtained from the marine environment databank MUDAB, v1.5.2 (https://geoportal.bafg.de/MUDABAnwendung/). These data were compared with the results of the OL-inlet samples as the latter are supposed to represent the concentration of the surrounding seawater. Notable differences between those can be attributed to contamination of seawater due to ship materials in the water supply system (corrosion and antifouling systems in pipelines, filters and sea chest) or at the sampling point. This is for instance the case for copper and zinc, which have been found by previous studies in high concentrations in the inlet water (Hermansson et al., 2021; Schmolke et al., 2020).

Regarding metals, they are found in very low concentrations (mostly in ng/l-range) in the sampled regions. The LOQ from the initial analyses were unsuitable for most of the OL-inlet samples as most results were <LOQ. Therefore, additional analyses were conducted by the laboratory of HEREON. This was not possible for ship 1 as there was no sample left. Where available, the results from the metals determination with lower LOQ were considered for this assessment and in Figure 13.

In Figure 13, differences between environmental (background) and OL-inlet concentrations are observed. Here, the use of logarithmic scale should be noted. Especially for copper, iron, mercury, nickel, vanadium and zinc the differences are noticeable. For copper and zinc, this observation was expected as commented above. For nickel, noticeable differences are only found in S2 and S4 and for vanadium in S2. These differences in S2 are commented below, while for S4 no hypothesis was formulated besides that it is a constituent of stainless steel. For mercury the observed differences in S3 and S4 cannot be explained as no source of mercury in the water supply system is known to us. However, it was considered the fact that the inlet water is uptake water from the surroundings with a maximum depth of 10 meters, while the values reported in the marine environment databank come from seawater samples with a depth between 10 and 40 meters. Since the largest source of mercury in the environment besides volcanic activity is coal combustion, both atmospheric input pathways, it is plausible that the levels reported in this study are elevated compared to concentrations in the entire water column. Unlike the other compounds, the iron concentration in OL-inlet was lower than the environmental concentrations; no explanation was found for it.

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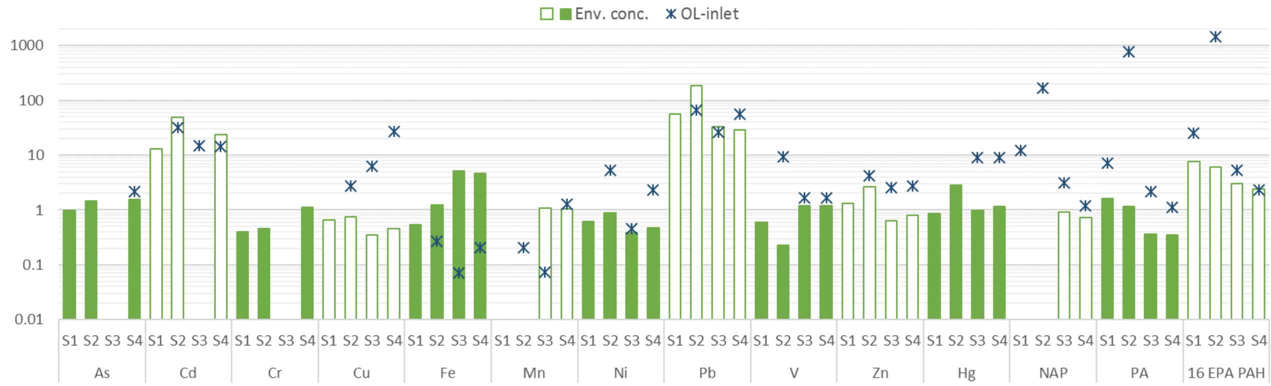
[4] LOQ varied depending on the different dioxin species. Toxicity of dioxins is calculated and summed up on the basis of the contents of the individual compounds and their respective factor, and then expressed as a so-called toxic equivalent (TEQ). The TEQ value corresponds to the toxicity of a comparable mass of 2,3,7,8 TCDD. The most common reference framework applied in environmental law to derive an I-TEQ (International-TEQ) is the 1988 I-TEF List by NATO/CCMS (UBA, 2010).

Regarding PAH, also many results were <LOQ. Therefore, only naphthalene, phenanthrene and the sum of 16 EPA PAH are depicted in Figure 13, where some differences between environmental (background) and OL-inlet concentrations were observed. As for nickel and vanadium, PAH concentrations in OL-inlet were extremely higher than expected from the environmental concentrations for S2. Because these compounds are the ones that are mostly enriched in the water during the scrubbing process, it is hypothesized that there was a cross contamination in the sampling point as during CL operation the same pipeline is used for the recirculated water.

This assessment demonstrates that the concentrations of pollutants in OL-inlet samples do not necessarily represent the environmental (background) concentrations of the surrounding seawaters, and actually in most cases the latter were exceeded.

Figure 13: Comparison of OL-inlet results with environmental (background) concentrations



Where concentrations of As, Cr, Cu, Fe, Mn, Ni, V and Zn are reported in µg/l and of Cd, Pb, Hg, NAP (naphthalene), PA (phenanthrene) and 16 EPA PAH in ng/l. A logarithmic scale is used in the diagram.

3.2 Emission factors

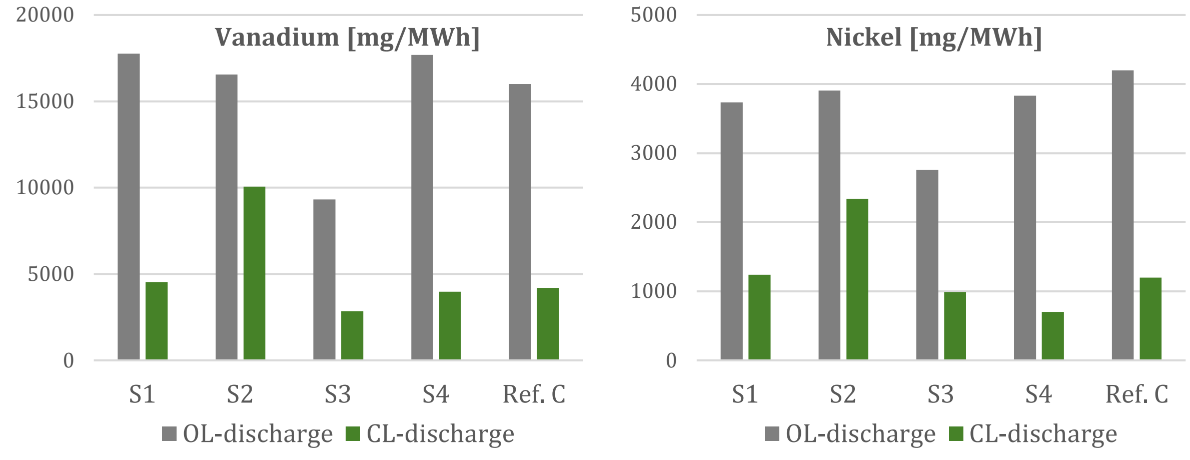
The emission factors (mass load of pollutant per energy output, EF) were calculated based on the concentrations of pollutants and the obtained specific flowrates (water flowrate per energy output). The full results can be found in Supplement B. Figure 14 and Figure 15 illustrate the differences in the emission factors between ships, compound types (metals and hydrocarbons) and scrubber operation modes. Average values from the literature are shown as reference. It should be noted that the inlet concentrations were not subtracted to obtain the emission factors; their contribution, however, is considered negligible for the selected compounds since the inlet and environmental concentrations are in a lower order of magnitude. For other compounds with lower concentrations, attention must be paid to this.

The results for vanadium and nickel agree to some extend with the average values reported by Hassellöv et al. (2020). For vanadium, the EF range from 9.3 to 17.8 g/MWh in OL and from 2.8 to 10.0 g/MWh in CL. For nickel, the EF range from 2.8 to 4.2 g/MWh in OL and from 0.7 to 2.3 g/MWh in CL. On average, the emission factors are 3.2 (vanadium) and 3.3 (nickel) times higher in OL than in CL operation.

The results for oil content and 16 EPA PAH show more variability and agree to a lesser extend with the average values reported by Hassellöv et al. (2020); for S1 and S2 the results are much higher. The possible explanations of these deviations are given in section 3.1.4. A logarithmic scale is used in Figure 15 to facilitate the comparison of all results. For oil content, the emission factors range from 7.5 to 121 g/MWh in OL and from 0.04 to 24 g/MWh in CL. For 16 EPA PAH, the emission factors range from 116 to 2987 mg/MWh in OL and from 2.3 to 519 mg/MWh in

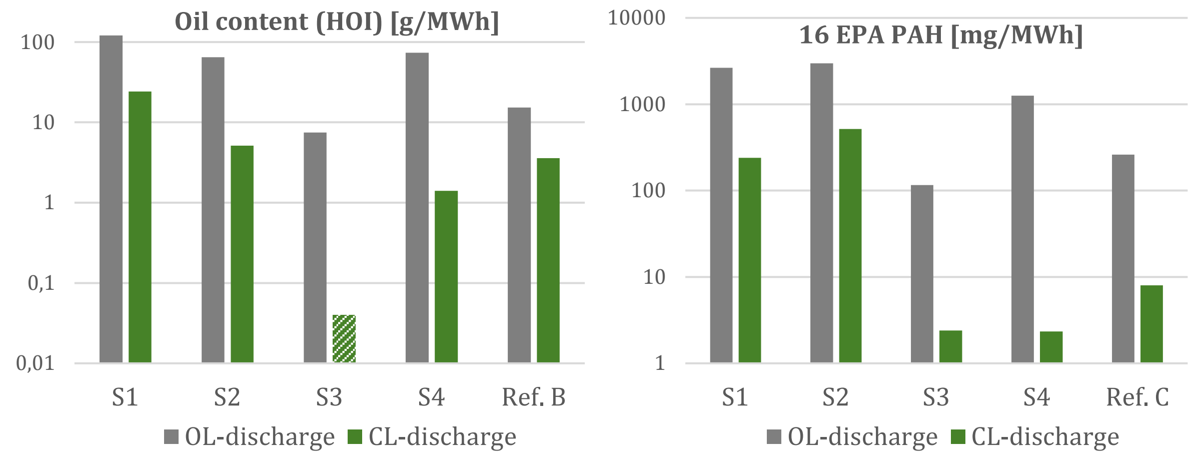
CL. For the extended list of PAH (not displayed in the figure), the emission factors range from 477 to 7051 mg/MWh in OL and from 42 to 1965 mg/MWh in CL. On average, the emission factors are 64 (oil content), 150 (16 EPA PAH) and 55 (extended list of PAH) times higher in OL than in CL operation. The assessment of the water treatment removal efficiencies (see section 3.3) can partly explain the significantly lower emission factors in CL-discharge water.

Figure 14: Vanadium and nickel emission factors in discharge water



Ref. C: Hassellöv et al. (2020).

Figure 15: Oil (HOI) and 16 EPA PAH emission factors in discharge water



Striped bars indicate that the result was below the limit of quantification (LOQ). In that case, the assigned value is LOQ/2. A logarithmic scale is used in both diagrams. Ref. B: Schmolke et al. (2020) and assumed average specific flowrates of 90 m^3/MWh and 0.45 m^3/MWh for OL and CL, respectively. Ref. C: Hassellöv et al. (2020).

In addition to the emissions caused by the scrubber discharge water, there are air emissions from the exhausts that could end up in the marine environment by natural processes (i.e. wet and dry deposition). This part is not covered by ImpEx because it is exclusively focused on the scrubber discharge water, hence, on the direct emissions to the marine environment. However, both water and air emissions from scrubber operation should be considered when comparing the different compliant options to regulation 14 of MARPOL Annex VI.

Winnes et al. (2018) measured in the exhaust gas from HFO combustion greater particle-bound PAH and metals emissions after scrubbing than from low-sulphur fuel oil (LSFO) combustion. Hermansson et al. (2021) found in general higher emission factors from combustion of HFO than of distillate fuels (MGO/MDO), especially for PAH, vanadium, nickel and iron. In addition, the authors compared the emissions from the use of HFO without scrubbing (prior to the entry into force of the SOx regulation) with the combination HFO and scrubber. They concluded that with the use of scrubbers the emissions become more local because great part of the exhaust gas pollutants end up in the scrubber discharge water so that the transportation and natural degradation processes (such as photochemical reactions) of pollutants in the atmosphere do not take place. Moreover, the use of scrubbers implies an introduction of additional pollution sources such as chromium from the corrosion of ship materials. Lastly, as compiled in the literature review (Marin-Enriquez et al., 2021), the scrubber operation requires higher fuel oil consumption.

3.3 Water treatment efficiency

In order to assess the removal efficiency of the different water treatment units of the sampled vessels in CL operation, the concentrations of selected compounds before and after treatment are used to calculate the water treatment efficiency. Figure 16 displays the results. Nickel (34 %) and vanadium (43 %) show on average lower removal rates than oil content (80 %) and 16 EPA PAH (66 %). Thus, hydrocarbons can be more easily removed than metals. This agrees with the study of Magnusson et al. (2018). They observed higher removal efficiencies for hydrocarbons than for metals, especially for the heavy fractions of hydrocarbons. This could be explained by the higher abundance of the hydrocarbons in particulate form, especially with higher molecular weight, in the water stream before the treatment when compared to metals. Detailed results of the present study showed higher pollutants removal in particulate form (69 % for nickel, 87 % for vanadium, 84 % for oil content and 69 % for 16 EPA PAH) than in dissolved form (<20 % for nickel, vanadium, oil content and 16 EPA PAH).

When comparing the water treatment efficiency in CL operation by ship, S1 and S4 show clearly higher values. Both ships make use of flocculant addition for the bleed-off treatment (see Table 3) in contrast to S2 and S3. A special case was S1, where the water treatment unit was operated almost permanently (even during OL operation) to clean bleed-off water from the process tank and to comply with the turbidity discharge criteria (<25 NTU/FNU); when turbidity was compliant, the water was pumped to the holding tank and discharged as required and where allowed.

Three ships were equipped with a treatment unit (hydrocyclone, see Table 3) in OL operation. Only in S4 it was possible to sample the water stream before treatment (S4/OL/BT). By comparing these results with the concentrations of the discharge water (S4/OL/BD), which is equivalent to the water stream after treatment, the removal efficiencies can be calculated. The results for the selected compounds (7 % for nickel, 5 % for vanadium, -109 % for HOI and -15 % for 16 EPA PAH[5]) indicate an inefficient treatment process. Thus, the usefulness of the water treatment step in OL operation is questioned. However, Ushakov et al. (2019) reported removal efficiencies in OL treatment (by means of hydrocyclone) of 45 – 55 % for hydrocarbons fractions, <15 % for PAH and ~10 % for metals. The treatment technologies (centrifugal separator and dissolved air flotation) typically used in CL operation are more efficient than the

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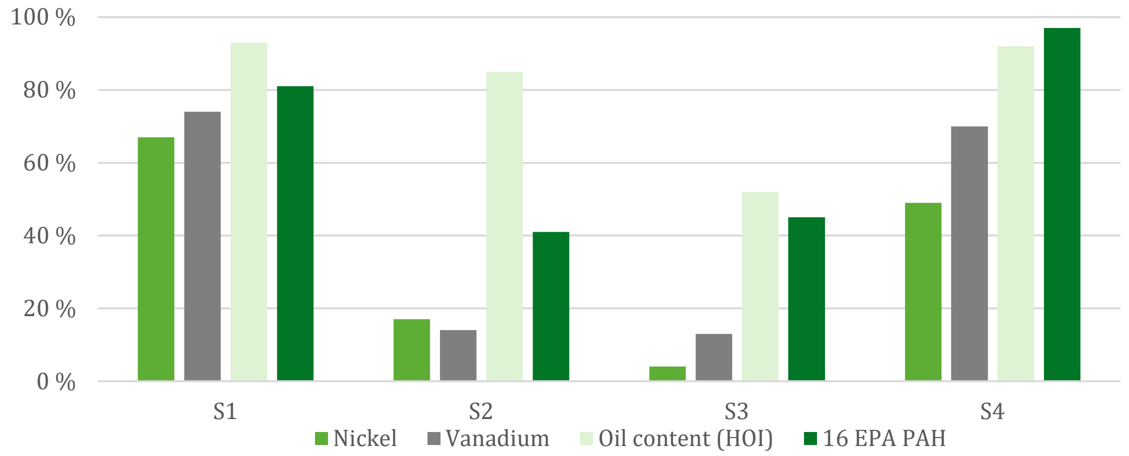
[5] The negative removal efficiencies indicate that the concentrations after treatment were higher than before treatment. It should not mean that the treatment step in OL increased the concentration of hydrocarbons (i.e. HOI and 16 EPA PAH), actually that seems to be unlikely. Instead, there could have been fluctuations in the engine combustion efficiency during the sampling period that could cause variations in the concentration of hydrocarbons. The process stream in OL before treatment was sampled 30 minutes later than after treatment. Another possible explanation is the fact that hydrocarbons were mainly present in particulate form, which require ideally isokinetic sampling conditions and those conditions were not given onboard.

hydrocyclone. Nevertheless, those technologies could not process the huge water flowrates in OL operation. In addition, at least for the hydrocarbon species, the particulate fraction is lower in the OL water stream before treatment than in CL.

The assessment above can partly explain the significant lower emission factors in CL-discharge water (see section 3.2).

Figure 16: Removal efficiency of water treatment systems in CL operation



HOI, hydrocarbon oil index.

3.4 Online monitoring

3.4.1 Online monitoring data

Irregularities and discrepancies in the online monitoring data have been reported by previous studies as compiled by Marin-Enriquez et al., (2021). Within ImpEx, the records from the online monitoring data of the sampled ships were collected and compared to the results of the *in situ* measurements conducted with own calibrated equipment (see Supplement B). Observations in this regard by ship are stated below:

- Ship 1 was equipped with a complete online monitoring system for OL and CL discharges. All recorded values (i.e. PAH_{phe}, pH and turbidity) are plausible. Apart from the turbidity in OL/IN, pH and turbidity records are similar to the measured values with own project equipment. Turbidity in OL/IN differed notably from the ImpEx measurement: the turbidity of the EGC Water Analyzer was 5.5 FNU and the recorded value from the onboard monitoring system was 0.4 FNU, which seems to be more plausible. The difference is most likely due to air bubbles in the EGC Water Analyzer, probably due to the measuring system loop installation. At the time of that sampling, the additional portable turbidimeter was unfortunately not available to verify that inconsistency. The PAH_{phe} records differed from the own measurements but had a good correlation. This observation was confirmed by the results of the parallel measurements, where the own and ship measurements followed the same trend. After consultation with the manufacturer of the EGC Water Analyzer, these differences could be caused by either: i) the scaling factor of the device, ii) dirt on the measuring window of the device or iii) the positioning (depth) of the device inside the flow-cell. It should be mentioned that both measurements used the same fluorometer model (enviroFlu from TriOS Mess- und Datentechnik).

- Ship 2 did not have monitoring equipment for CL discharges; it only included a turbidity sensor downstream the separator (CL/AT). It should be noted that the discharge water from the holding tank is mixed with the OL discharge and monitored as a mixture (see section 4.2). Generally, the recorded values from the online monitoring (i.e. PAH_{phe}, pH and turbidity) were plausible but with some particularities. The pH in OL/IN (7.1) was too low for seawater conditions and in OL/OU the pH was around two units higher than the project measurements. Either the pH sensors are not properly calibrated or the settings have been incorrectly adjusted (e.g. wrong offset value). The turbidity records in OL were inconsistent (OL/IN resulted higher than OL/OU) and differed from the own measurements. The turbidity records in CL samples reflected the high turbidity in those samples as confirmed by the own measurements. The PAH_{phe} records for OL/IN and OL/BD are relatively close to the own measurements.

- Ship 3 did not have monitoring equipment for CL discharges; it only included a turbidity sensor downstream the separator (CL/AT). Some of the recorded values (i.e. PAH_{phe}, pH and turbidity) were not plausible. The pH in OL/OU was close to the own measured value, however in OL/IN (8.6) the recorded value was relatively high for seawater conditions. The turbidity records in OL were judged as incorrect as for OL/IN turbidity was negative and turbidity of OL/BD sample was much higher (i.e. about four times) than the own measurements. There were no available records for the CL operation since the discharge water from the holding tank is mixed with the OL discharge and monitored as a mixture (see section 4.2). The PAH_{phe} record for OL/IN was a negative value (not plausible) and OL/BD was close to the own measurement. Negative values can occur if the software of the measuring device does not include a post-processing correction or if the offset value is adjusted.

- Ship 4 was equipped with a complete monitoring system for OL and CL discharges. Most of the recorded values (i.e. PAH_{phe}, pH and turbidity) were plausible but with some exceptions. The pH records were close to the own measured values. Apart from CL/AT, the turbidity records differed from the own measurements; OL/IN was a negative value (but close to zero) and OL/OU and CL/OU were very low. The PAH_{phe} records for OL samples were plausible but differed from the own measurements, while the records in CL operation were extremely low (not plausible).

In summary, the online monitoring systems of the ships measured different values as compared to project own measurements. The online monitoring data also showed inconsistencies in at least one of the parameters to be monitored. These findings corroborated the issues reported by other studies and put into question the reliability of onboard online monitoring for scrubber water discharges. Periodic cleaning, calibration and maintenance are essential for accurate monitoring. The correct installation of the sensors by following the manufacturer’s specifications is also important for this complex measuring equipment.

3.4.2 PAH_{phe} as surrogate parameter for oil content

A special case is the monitoring of PAH_{phe}. The reasons for this are not only from technical but also from regulatory nature. First of all, to our knowledge PAH_{phe} is exclusively used for the regulation of scrubber discharges within the IMO. The definition of PAH_{phe} and the related measuring particularities (i.e. excitation and detection wavelengths) were not described in the previous versions of the 'EGCS Guidelines'. Consequently, there was room for interpretation for the measurement method and how the results should be reported. Within the ImpEx project it was found that monitoring systems report PAH$_{phe}$ non-uniformly, either:

- the raw measured value,
- the measured value corrected by turbidity,
- the measured value corrected by a factor to represent the sum of 16 EPA PAH or
- the measured value with both corrections.

In addition, the optical measurement of PAH$_{phe}$ for online monitoring is not simple. Only dissolved PAH can be measured, the particulate fraction is overlooked. Also the presence of suspended particles interfere with the measurement (Linders et al., 2019). Therefore, the monitoring of CL-discharge water is more challenging than for OL, based on the observed higher suspended solids content and the dominance of PAH in particulate form.

PAH$_{phe}$ was proposed as a surrogate parameter for oil content, hence its discharge limit aims to protect the marine environment from discharges of oily residues as compiled by Marin-Enriquez et al. (2021). Considering the points mentioned above, the sense of purpose of PAH$_{phe}$ monitoring was assessed by comparing the project own measurements of PAH$_{phe}$ with the laboratory results of phenanthrene, sum of 16 EPA PAH and oil content that are displayed in Table 13.

Table 13: Comparison of PAH$_{phe}$ project measurements with laboratory results

Parameter	S1			S2			S3			S4		
	OL-inlet	**OL-discharge**	**CL-discharge**	**OL-inlet**	**OL-discharge**	**CL-discharge**	**OL-inlet**	**OL-discharge**	**CL-discharge**	**OL-inlet**	**OL-discharge**	**CL-discharge**
PAH$_{phe}$ [µg/l] [i.]	5.8	39	60	6.6	54	75	3.6	6.9	21	3.9	23	44
PHEN [µg/l]	0.007	11.0	30	0.76	18.0	88	0.002	0.64	3.7	0.001	6.7	7.3
16 EPA PAH [µg/l]	0.025	28	79	1.5	56	150	0.005	1.7	6.9	0.002	17.4	11.6
Oil content [mg/l]	<0.1	1.3	8.1	0.14	1.2	1.5	<0.1	0.11	<0.1	<0.1	1.0	7.1

PHEN: phenanthrene; OL-inlet: OL/IN; OL-discharge: OL/BD; CL-discharge: CL/OU.

i. Raw value from the project measurements (not from the onboard online monitoring).

Figure 17 displays the results of the parameters mentioned above in order to assess the suitability of PAH$_{phe}$ as monitored parameter in the discharge water of OL and CL. To increase the information base, the data from the previous scrubber project conducted by BSH (Schmolke et al., 2020) were considered too. The graphs in Figure 17 include a trend line, the regression line equation and the coefficient of determination (R^2). It can be observed that phenanthrene, 16 EPA PAH and oil content are strongly related to PAH$_{phe}$ in OL-discharge. In fact, the PAH$_{phe}$ values are equivalent to the sum of 16 EPA PAH with an offset close to 7 (i.e. 16 EPA PAH = 1.06 · PAH$_{phe}$ – 7.32, see Figure 17-C). Oil content seems to be 30 times higher than PAH$_{phe}$ and a concentration of 1 mg/l is thus reached with a PAH$_{phe}$ concentration of around 40 µg/l.

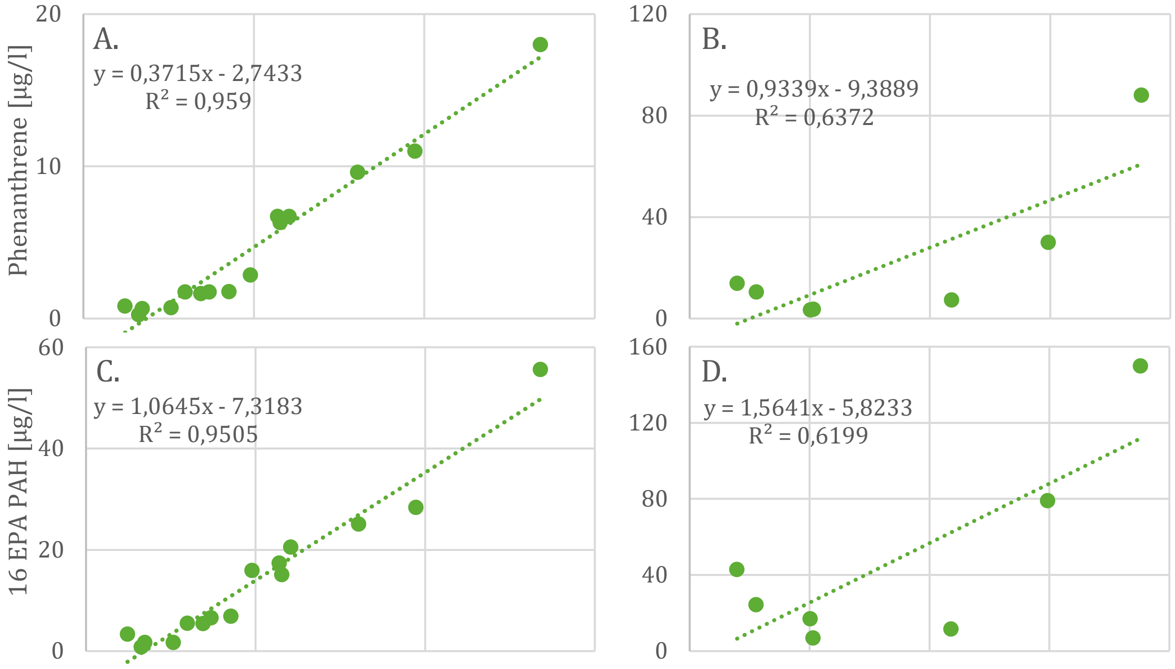
In CL-discharge, there is weaker relation of phenanthrene and 16 EPA PAH with PAH_{phe}; while no relation was obtained with oil content (see Figure 17). As mentioned above, higher suspended solids content and the dominance of PAH in particulate form make difficult the monitoring of CL-discharge water. Another reason might be the discoloration (blackening) of the water, which hamper the optical UV measurement. By comparing the laboratory results of oil content with 16 EPA PAH and phenanthrene concentrations in CL-discharge, a plot (not shown here) with scattered points producing a regression line with negative slope is formed, similar to Figure 17-F. Thus, the problem is not only the online monitoring device for PAH_{phe} but also the fact that there was no correlation of oil content with PAH species in CL-discharge samples.

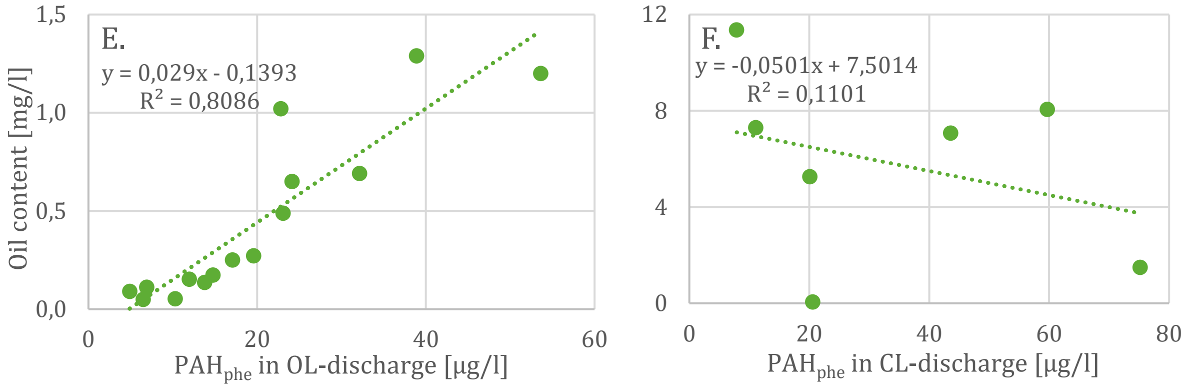
As conclusion, PAH_{phe} is an excellent surrogate parameter for oil content in OL-discharge water but not in CL-discharge.

It should be noted that all PAH_{phe} measurements in the used dataset were conducted with the same fluorometer model. Data from OL-inlet samples were not considered as in this measuring range the fluorometer seems not to be accurate enough (LOD: 0.5 µg/l) besides the measuring interference of natural occurring species in seawater such as humic substances that generate a signal. Not all scrubber systems include PAH_{phe} monitoring in the water inlet because the normal concentrations of PAH in seawater are negligible compared to the limit value for the discharge water.

Figure 17: Comparison of PAH_{phe} with laboratory results in discharge water

Comparison of PAH_{phe} with phenanthrene, 16 EPA PAH and oil content in OL-discharge (A., C. and E.) and in CL-discharge water (B., D. and F.).





PAH_{phe}, Polycyclic aromatic hydrocarbons as phenanthrene equivalent (raw measured value). The equations describe the regression line.

3.4.3 Technical possibilities for monitoring of nitrogen compounds

Nitrate and nitrite were measured in water samples from S3 and S4 with the sensor OPUS-UV and compared with the laboratory results to evaluate the technical feasibility for monitoring of those parameters in scrubber discharge water.

The online monitoring of nitrate and nitrite is already in place for onshore applications (e.g. wastewater, drinking water and surface water including marine water). Due to the unexplored complex matrix (e.g. high salinity, oil residuals and suspended solids) of the scrubber water samples, the evaluation of the spectral data was challenging. Here, the high concentrations of sulphate and sulphite interfered with the measurement. This task was conducted by a specialist from the manufacturer of the sensor (TriOS).

Only in CL samples nitrate and nitrite concentrations were possible to obtain. The selected optical path length was unsuitable for the very low concentrations in OL samples. The results in the CL samples (not shown in this report) are plausible and in the same order of magnitude as the laboratory results. The selection of a more suitable optical path length in the sensor could have led to more accurate results even in the OL samples.

As a conclusion, the technical feasibility for onboard online monitoring of nitrates was demonstrated. However, no further efforts will be undertaken on this topic. As indicated above, nitrates might not be relevant in conventional scrubber systems (see section 3.1.2). In addition, the ‘EGCS Guidelines’ do not require the onboard monitoring of these compounds; only nitrate should be analyzed during the commissioning and prior to each renewal survey.

3.5 Fuel and lube oil composition

Fuel and, to a lesser extent, lube oil contribute to the presence of pollutants in the discharge water (Gadd, 2020). In order to evaluate the potential sources of pollutants found in the water samples and exclude possible contamination issues (e.g. due to sampling point fittings), the composition of fuel and lube oils used on board the sampled vessels was determined. The complete results of the fuel and lube oil composition can be found in Supplement B.

Table 14 presents the results for selected compounds in the fuel oil samples compared to typical concentrations as reported in the literature. It is known that the quality of HFO found in the global market can vary significantly. The results of the sampled fuel oils, however, are close to the average values reported in the literature. The sulphur content ranged from 2.1 to 3.2 %. Iron, nickel, vanadium and zinc were the metals with results above the LOQ. The LOQ for all metals was 1 mg/kg, except for mercury (1 µg/kg). In general, lube oil samples showed low concentration of metals, except by zinc (350 – 500 mg/kg), along with nickel and vanadium, which were found in the fuel oil at high concentrations. These may have accumulated after continuous use of the lube oil in the combustion system.

Table 14: **Fuel oil composition**

Compounds	S1	S2	S3	S4	Literature
Sulphur [% m/m]	2.1 %	2.1 %	3.2 %	2.2 %	2.7 %[a.]
Fe [mg/kg]	38	39	6	70	15[b.]
Ni [mg/kg]	46	49	41	62	31[b.]
V [mg/kg]	186	200	120	248	112[b.]
Zn [mg/kg]	1.0	2.0	<1.0	2.0	1.8[b.]
16 EPA PAH [mg/kg]	3736	3154	2799	7370	3227[c.]

Fe, iron; Ni, nickel; V, vanadium; Zn, zinc.

a. ExxonMobil (nd); b. Hermansson et al. (2021); c. Uhler et al. (2016).

Based on the results above and on the SFOC during OL operation (reported in Table 3), the potential emission factors of metals from fuel oil combustion were calculated and compared to the emission factors from OL discharge water (see Table 15). For nickel and vanadium the results are plausible and within a narrow range, indicating the fuel oil as the main source for these metals in the discharge water. Assuming fuel oil as the only source of pollutants found in the discharge water, 28 – 41 % of nickel and 33 – 47 % of vanadium from the fuel ends up in the OL-discharge water. Kjølholt et al. (2012) reported that the scrubbing process can capture 23 % of nickel and 32 % of vanadium. Iron is also found in relevant concentrations in the fuel oil; however, the relation with the concentrations found in the discharge water is not that clear as for nickel and vanadium. Here, the corrosion of ship's and scrubber system's materials could be a significant source of iron in the discharge water as well. That could be the case for samples from ship 3 that resulted in extreme high values for iron. Similarly, and with lower values, for zinc no relation can be found between discharge water and fuel oil composition. Here, corrosion of metal components and lube oil could be relevant sources of zinc. In Table 15, emission factors are shown also for pollutants, whose concentrations were reported as <LOQ.

Table 15: **Influence of fuel oil composition on discharge water**

Comparison for selected metals of emission factors (g/MWh) of OL-discharge samples with potential emission factors (g/MWh) from fuel oil combustion.

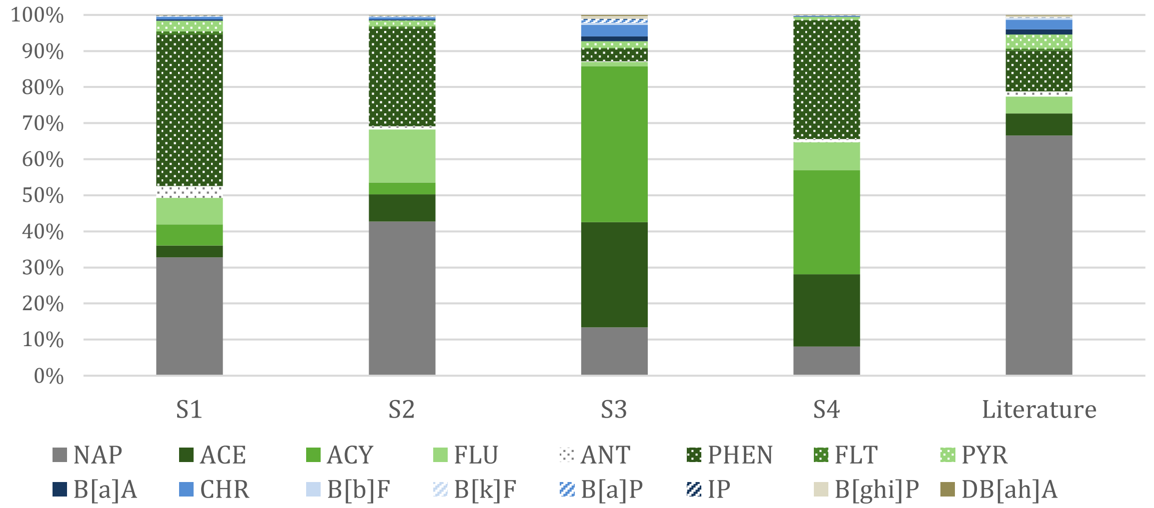
Comp.	S1			S2			S3			S4		
	EF_{OL}	EF_{FO}	%	EF_{OL}	EF_{FO}	%	EF_{OL}	EF_{FO}	%	EF_{OL}	EF_{FO}	%
Fe	<5.6	8.0	<70 %	4.8	8.4	57 %	40.9	1.0	4164 %	4.2	15.3	27 %
Ni	3.7	9.7	38 %	3.9	10.6	37 %	2.8	6.7	41 %	3.8	13.6	28 %
V	17.8	39.4	45 %	16.6	43.3	38 %	9.3	19.6	47 %	17.7	54.3	33 %
Zn	<2.8	0.21	<1323 %	<0.97	0.43	<224 %	<1.2	<0.16	NA	<1.3	0.44	<297 %

EF_{FO}, potential emission factor from fuel oil combustion; EF_{OL}, emission factor from OL-discharge; %, ratio of EF_{FO}/ EF_{OL} as a percentage; Fe, iron; Ni, nickel; V, vanadium; Zn, zinc.

The content of 16 EPA PAH in the fuel oil samples were between 0.3 and 0.7 % (see Table 14). Figure 18 shows the PAH concentrations among the fuel oils with notable variations, which is expected according to Uhler et al. (2016). Naphthalene and phenanthrene show the highest concentration. The abundance of PAH decreases with increasing molecular weight. PAH of four or more rings resulted <LOQ in some samples. While only the concentration of 16 EPA PAH was determined, it is assumed that the presence of alkylated PAH is significant, especially of alkyl-naphthalenes. Uhler et al. (2016) analysed the composition of 71 different IFO 380 fuel oils worldwide and determined the average concentration of the 16 EPA PAH by 3227 mg/kg and of the total 54 measured PAH and alkylated PAH by 27171 mg/kg.

The concentration of 16 EPA PAH in lube oil samples was very low; most of the results are <LOQ. This agrees with the information reported by Uhler et al. (2016). This study mentions that the lube oils are manufactured for removal of aromatic compounds to improve the performance properties of the oil and that the presence of PAH in used lube oils is due to the mixing with unburnt fuel oil and, to a lesser extent, formed by excessive heating.

Figure 18: 16 EPA PAH distribution in fuel oil



Literature: Uhler et al. (2016).

Abbreviations: ACE, acenaphthene; ACY, acenaphthylene; ANT, anthracene; B[a]A, benz[a]anthracene; B[a]P, benzo[a]pyrene; B[b]F, benzo[b]fluoranthene; B[k]F, benzo[k]fluoranthene; B[ghi]P, benzo[ghi]perylene; CHR, chrysene; DB[ah]A, dibenz[a,h]anthracene; FLT, fluoranthene; FLU, fluorene; IP, indeno[1.2.3-cd]pyrene; NAP, naphthalene; PHEN, phenanthrene; PYR, pyrene.

3.6 Ecotoxicological effects of water samples

3.6.1 Whole effluent toxicity

For the purpose of this report, we simplified the presentation of the WET testing results by only showing the results of the undiluted (100 %) samples. There is, however, an exception with the results of the copepod tests because the salinity of the undiluted samples of the CL samples of the ships S3 and S4 proved to be too high and thus, outside the acceptable range of the copepods. Therefore, it was decided not to test the undiluted samples and start only with the 1:2 dilution, which corresponds to a concentration of 50 %.

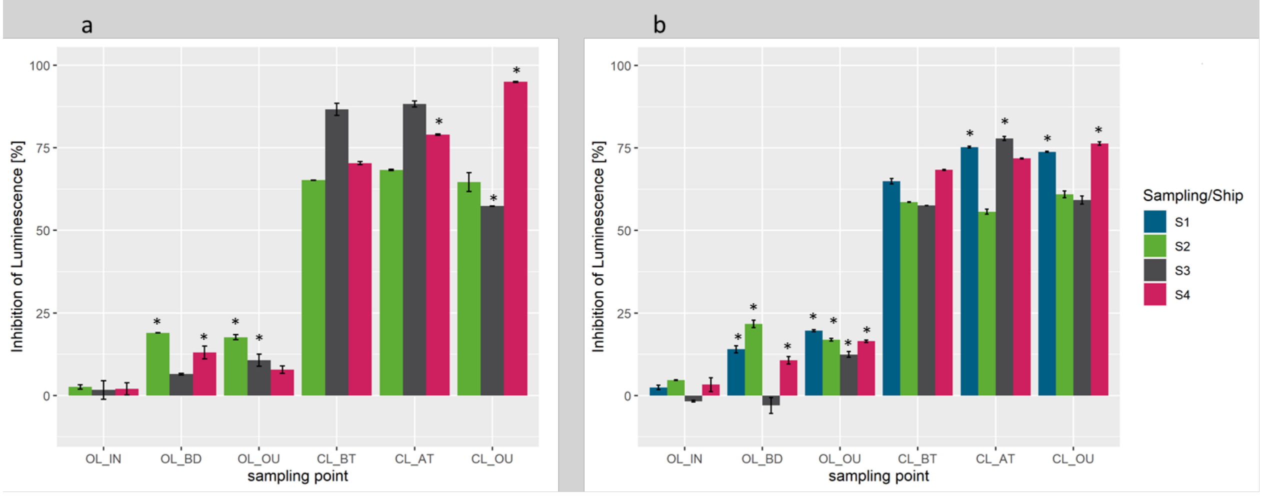
It should also be noted that it was necessary to raise the pH value to 7.0 in two thirds of the OL samples and in one third of the CL samples.

3.6.1.1 Luminescent bacteria

The results of the luminescent bacteria tests (Figure 19) show that the inhibition of the luminescence of the bacteria was several times higher in the CL than in the OL samples. Figure 19a depicts the results of the BfG and Figure 19b shows the results of Nowak in comparison. The samples of S1 were not measured at the BfG due to insufficient sample volumes.

Overall, the luminescence inhibition of the OL samples remained on average below 20 % in both laboratories and ranged from 57 % to 95 % at the BfG and from 55 % to 79 % at Nowak in the CL samples. The inhibition values vary, in some cases significantly, between the ships whereby the differences are more similar between the laboratories in the CL than the OL samples. The most prominent difference between the laboratories can be seen between S3 and S4 for sample CL/BT.

Figure 19: Inhibitory effect of scrubber water samples on the luminescence emission of *Aliivibrio fischeri*

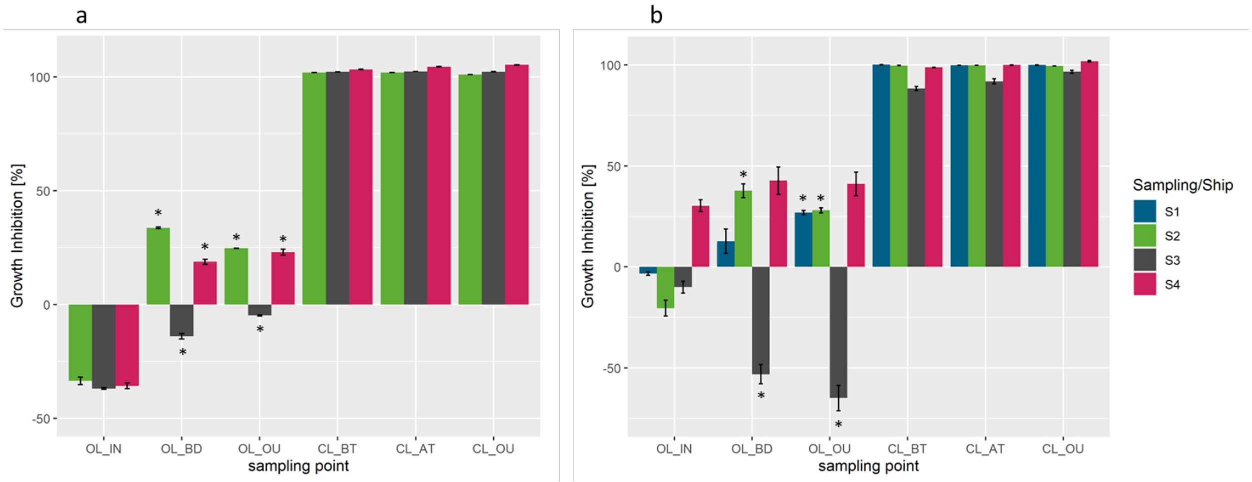


Inhibition of luminescence (in %) by undiluted (100 %) scrubber water samples: a. results of the BfG, b. results of Nowak. Depicted are the mean values ± standard deviation for n = 2 (technical replicates). Sampling codes as described in Table 2; here, OL/BD in S4 corresponds to OL/BT. Asterisks denote significant differences (ANOVA with Tukey post-hoc test ($p<0.001$)) of the OL samples after the scrubber (OL/BD and OL/OU) compared to the sample before the scrubber (OL/IN) and of the CL samples after treatment (CL/AT and CL/OU) compared to the sample before treatment (CL/BT) on each ship.

3.6.1.2 Marine algae

As with the luminescent bacteria, the marine algae tests show significant differences between the OL and the CL samples. The CL samples were more than twice as toxic as the OL samples (Figure 20), reaching inhibition values of 87 % (Nowak) und 105 % (BfG). In case of the OL samples, differences in the effect pattern of the individual samples can also be seen, but there are also differences in the effect sizes between the results of the BfG (Figure 20a) and Nowak (Figure 20b). However, both laboratories showed consistently that the growth of the algae was promoted in all OL/IN samples, but this growth promotion exceeded -25 % only at the BfG. The other two OL sampling points (process streams after scrubbing) showed growth inhibition for sampling S1, S2 and S4, but growth promotion for sampling S3. At the BfG, this growth-promoting effect indicated a decreasing trend along the scrubber system (Figure 20a), whereas this effect increased in the Nowak laboratory (Figure 20b). One possible explanation for the growth promoting effect of the OL samples of S3 may be the iron content. The dissolved iron concentration of the OL/BD sample of S3 was for instance 548 µg/L and thereby more than ten times higher than for S1, S2 and S4. Iron is an essential element for algal growth, and it has been shown for *P. tricornutum* that the growth of the diatoms is positively correlated with the iron content in the environment, presumably due to a stimulating effect of the iron on photosynthesis (Zhao et al., 2018).

Figure 20: Growth inhibitory effects of scrubber water samples on *Phaeodactylum tricornutum*

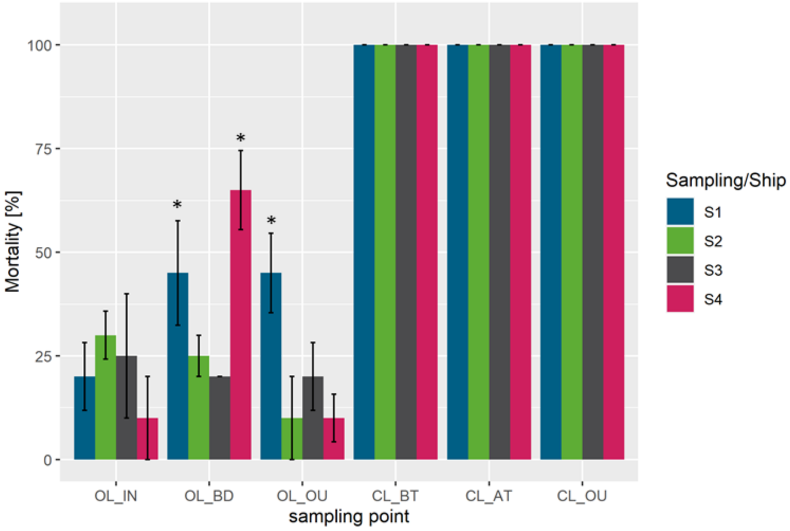


Percent growth inhibition (in %) by undiluted (100 %) scrubber water samples in the marine algae test: a. results of the BfG, b. results of Nowak. Negative values indicate growth promotion. Shown are the mean values ± standard deviation for n = 3 (technical replicates). Sampling codes as described in Table 2; here, OL/BD in S4 corresponds to OL/BT. Asterisks denote significant differences (ANOVA with Tukey post-hoc test ($p<0.001$)) of the OL samples after the scrubber (OL/BD and OL/OU) compared to the sample before the scrubber (OL/IN) and of the CL samples after treatment (CL/AT and CL/OU) compared to the sample before treatment (CL/BT) on each ship.

3.6.1.3 Copepods

In line with the results of the luminescent bacteria and the marine algae, the undiluted (for S1 and S2) and 1:2 diluted (for S3 and S4) CL samples had on average a much higher toxicity on the copepods than the OL samples. All copepods were found dead after 48 h in the CL samples. The OL samples showed differences in mortality between the samplings before (OL/IN) and after (OL/BD and OL/OU) scrubbing, some of which were significant (indicated by asterisks over the bars in Figure 21). The standard deviations between the technical replicates of the OL samples in the copepod testing were higher than for the luminescent bacteria or marine algae.

Figure 21: Acute lethal toxicity of scrubber water samples on *Acartia tonsa*



Mortality after 48 hours (in %) caused by scrubber water samples in the copepod tests. In case of CL samples of S3 and S4, a 1:2 dilution (50 %) of the samples was required (due to high salinity values), all other bars show the effect of undiluted (100 %) samples. Shown are the mean values ± standard deviation for n = 4 (technical replicates). Sampling codes as described in Table 2; here, OL/BD in S4 corresponds to OL/BT. Asterisks denote significant differences (ANOVA with Tukey post-hoc test ($p<0.001$)) of the OL samples after the scrubber (OL/BD and OL/OU) compared to the sample before the scrubber (OL/IN) and of the CL samples after treatment (CL/AT and CL/OU) compared to the sample before treatment (CL/BT) on each ship.

3.6.1.4 Summary of WET results

In order to rate the relevance of the individual WET tests and rank the scrubber water samples according to their ecotoxicological potential, we combined the results, determined the pT_{max} value for each sample and assigned it to a toxicity category according to Table 7. This summary of the WET results and ecotoxicity categorisation is depicted in Table 16 and Table 17.

Table 16: Summary of the physico-chemical parameters, results of the WET tests shown as pT-values and toxicity categories for the OL scrubber water samples

Sample	Laboratory	Physico-chemical parameters pH	 NH_4^+-N [mg/l]	 O_2 after aeration [mg/l]	 EC [mS/cm]	 Salinity [PSU]	Marine algae test DIN EN ISO 10253 pT-value	Luminescent bacteria test DIN EN ISO 11348- pT-value	Copepods test ISO 14669 : 1999 pT-value	pT$_{max}$	**Toxicity category**
S1/OL/IN	Nowak / Noack	8.0	<0.5	9.2	14	8.2	0	0	5	5	Highly toxic
S2/OL/IN	BfG	8.1	<1	8.9	13	7.5	0	0	1	1	Practically non-toxic
	Nowak/Noack	8.1	<0.5	9.6	13	7.3	0	0			
S3/OL/IN	BfG	8.2	<1	10.6	48	30.7	0	0	2	2	Slightly toxic
	Nowak/Noack	8.2	1	11.9	50	32.9	0	0			
S4/OL/IN	BfG	8.3	<1	11.0	35	31.9	0	0	0	3	Moderately toxic
	Nowak/Noack	8.3	1	11.7	48	31.4	3	0			
S1/OL/BD	Nowak / Noack	*3.5*	<0.5	7.6	15	8.5	0	0	5	5	Highly toxic
S2/OL/BD	BfG	*3.2*	<1	8.3	13	7.7	2	0	3	3	Moderately toxic
	Nowak/Noack	*3.0*	<0.5	8.8	13	7.6	3	1			
S3/OL/BD	BfG	*2.9*	<1	5.0	49	30.5	0	0	1	1	Practically non-toxic
	Nowak/Noack	*2.7*	1	10.5	49	31.7	0	0			
S4/OL/BD	BfG	*3.6*	<1	9.2	34	30.4	0	0	2	2	Slightly toxic
	Nowak/Noack	*3.3*	1	8.9	48	31.2	2	0			
S1/OL/OU	Nowak / Noack	*3.6*	<0.5	8.8	18	10.4	1	0	4	4	Considerably toxic
S2/OL/OU	BfG	*3.6*	<1	9.0	14	7.9	1	0	0	2	Slightly toxic
	Nowak/Noack	*3.4*	<0.5	9.0	13	7.8	2	0			
S3/OL/OU	BfG	*4.0*	<1	10.0	48	30.4	0	0	1	1	Practically non-toxic
	Nowak/Noack	*4.2*	1	11.6	49	31.7	0	0			
S4/OL/OU	BfG	*3.5*	<1	7.6	36	31.7	1	0	0	1	Practically non-toxic
	Nowak/Noack	*3.4*	< 0.5	8.1	47	30.4	1	0			

The pH values shown in italics were adjusted to 7.0 ± 0.2. Beside ship S1, the marine algae test and luminescent bacteria test were conducted at Nowak as well as BfG, thus two results are shown for S2, S3 and S4. The copepod test is not established at the BfG, so it was only performed by the contract laboratory Dr. Noack. The toxicity class was determined by the most sensitive test (pT$_{max}$). Sampling codes as described in Table 2; here, S4/OL/BD corresponds to S4/OL/BT. EC means electrical conductivity.

The samples from the first ship (S1) showed the highest toxicity among the OL-samples, leading to toxicity categories 4 and 5 (considerably to highly toxic). Worth mentioning here is that the results for the copepods were responsible for this classification; marine algae and bacteria showed pT-values of 1 and 0 and thus, no effects for these samples. For the other ships, only two other OL samples (S4/OL/IN and S2/OL/BD) showed moderate toxicity in the marine algae test and were therefore classified as moderately toxic. The reason for the high copepod toxicity of the OL/IN and OL/BD water samples of S1 is not clear but may suggest some contamination from the inlet pipes which specifically affected the copepods and not the other organisms.

Although the scrubber discharge samples of the OL operation exhibited practically no or at maximum, considerable toxicity to the three organisms tested, the samples should not be considered harmless. It should be noted that the WET tests carried out in the present study only reflect acute toxic effects. Chronic WET test were not part of the study. Also, effects of low pH are not reflected in the WET tests, since the pH was adjusted to 7.0 ± 0.2 in all OL/BT and OL/OU samples due to deviations from the acceptable range according to the standard methods.

Table 17: Summary of the physico-chemical parameters, results of the WET tests shown as pT-values and toxicity categories for the CL scrubber water samples

Sample	Laboratory	Physico-chemical parameters					Marine algae test DIN EN ISO 10253	Luminescent bacteria test DIN EN ISO 11348-	Copepods test ISO 14669 : 1999	pT_{max}	**Toxicity category**
		pH	NH_4^+-N [mg/l]	O_2 after aeration [mg/l]	EC [mS/cm]	Salinity [PSU]	pT-value	pT-value	pT-value		
S1/CL/BT	Nowak / Noack	*10.5*	<0.5	*<1*	23	14.1	4	4	6	6	Extremely toxic
S2/CL/BT	BfG	7.5	<1	5.7	15	8.7	6	4	5	6	Extremely toxic
	Nowak/Noack	8.2	<0.5	*0.3*	15	8.5	5	4			
S3/CL/BT	BfG	*2.9*	2	*3.4*	70	46.7	7	2	5	6	Extremely toxic
	Nowak/Noack	*2.7*	4	5.9	60	50.6	5	3			
S4/CL/BT	BfG	*4.4*	19	6.1	61	55.2	>6	4	8	6	Extremely toxic
	Nowak/Noack	*4.5*	29	9.5	59	39.0	8	4			
S1/CL/AT	Nowak / Noack	6.1	0.67	5.0	23	13.9	5	5	6	6	Extremely toxic
S2/CL/AT	BfG	7.7	<1	*2.3*	15	9.0	6	4	4	6	Extremely toxic
	Nowak/Noack	8.4	<0.5	*0.3*	15	8.6	5	4			
S3/CL/AT	BfG	*2.9*	2	*1.4*	71	47.1	7	3	6	6	Extremely toxic
	Nowak/Noack	*2.6*	3	5.1	68	48.0	5	2			
S4/CL/AT	BfG	7.0	20	8.6	61	53.8	>6	3	4	6	Extremely toxic
	Nowak/Noack	7.0	32	10.7	58	38.7	8	3			
S1/CL/OU	Nowak / Noack	6.9	<0.5	6.2	23	14	5	4	6	6	Extremely toxic
S2/CL/OU	BfG	*4.9*	<1	8.2	17	10.2	6	5	5	6	Extremely toxic
	Nowak/Noack	*3.4*	<0.5	5.8	18	10.5	5	4			
S3/CL/OU	BfG	7.0	1	8.0	72	47.9	7	2	8	6	Extremely toxic
	Nowak/Noack	7.4	4	10.6	67	48.4	5	3			
S4/CL/OU	BfG	6.8	26	*0.3*	64	54.2	>6	4	4	6	Extremely toxic
	Nowak/Noack	7.3	40	6.7	59	39.2	7	4			

The pH values shown in italics were adjusted to 7.0 ± 0.2. Some samples did not reach the minimum oxygen concentration of 5 mg/L required for the test organisms even after long aeration; these values are also shown in italics. Beside ship S1, the marine algae test and luminescent bacteria test were conducted at Nowak as well as BfG, thus two results are shown for S2, S3 and S4. The copepod test is not established at the BfG, so it was only performed by the contract laboratory Dr. Noack. The toxicity class was determined by the most sensitive test (pT_{max}). Sampling codes as described in Table 2. EC means electrical conductivity

Generally, the effects of the CL samples were much higher than the OL samples. All examined CL samples were categorised as extremely toxic and thus, assigned to the highest toxicity category 6. Responsible for this ranking were mostly the copepods, which proved to be one of the most sensitive species, followed by the marine algae. All CL samples reached a maximum pT_{max} value of ≥ 6 in either the algae or the copepod test.

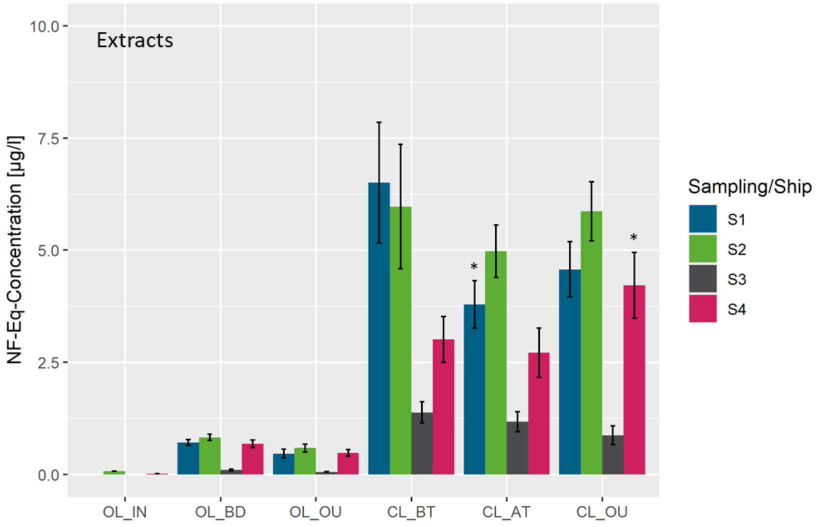
There was no difference in the overall toxicity between the sampling points in CL, suggesting that the treatment of the scrubber bleed-off water on these ships was ineffective in lowering the toxic load. There is no apparent relationship between this observation and the results of the efficiency of pollutants removal (Figure 16). Looking at the results with the different test organisms, the pT-values of the copepod tests for ship 2 and 4 decreased after treatment (from CL/BT to CL/AT), which may indicate that the treatment on these two ships was able to remove a toxicant from the scrubber bleed-off water the copepods were specifically sensitive to. However, the toxicity toward the marine algae and luminescent bacteria did not change from before to after treatment, except for a minor decrease of the pT-value of the luminescent bacteria test on ship 4 (from CL/BT to CL/AT).

3.6.2 Specific toxicity tests

3.6.2.1 Yeast dioxin screening

The results of the YDS (Figure 22) show the binding affinity to the hAHR of the extracts of the scrubber water samples and therefore the dioxin-like effects, expressed as NF-eq. Concentration factors (due to the SPE) were accounted for, therefore the NF-eq values correspond to the undiluted samples.

Figure 22: Dioxin-like effects of scrubber water samples in recombinant yeast, *Saccharomyces cerevisiae*



Binding affinity of the scrubber water samples (extracts) for the hAHR in the YDS. Depicted are β-naphthoflavone equivalence concentrations (µg/l), shown as mean values ± standard deviation for n=3 (test replicates). Sampling codes as described in Table 2; here, OL/BD in S4 corresponds to OL/BT. Asterisks denote significant differences (ANOVA with Tukey post-hoc test ($p<0.001$)) of the OL samples after the scrubber (OL/BD and OL/OU) compared to the sample before the scrubber (OL/IN) and of the CL samples after treatment (CL/AT and CL/OU) compared to the sample before treatment (CL/BT) on each ship.

As with the luminescent bacteria, algae and copepods, the effects of the CL samples in the YDS were higher (up to nine times) than the OL samples, at least for S1, S2 and S4. In case of the S3 samples, the NF-eq concentrations were generally lower and there was no significant difference between the OL and the CL samples. This is coherent with the results of the chemical analysis where oil content and 16 EPA PAH concentration were lower for S3 (Figure 8) than for the other ships. The highest NF-eq concentrations were determined for the CL samples of S1 and S2. These samples featured higher concentrations of the extended list of PAH in the dissolved fraction than the other two ships (see Supplement B).

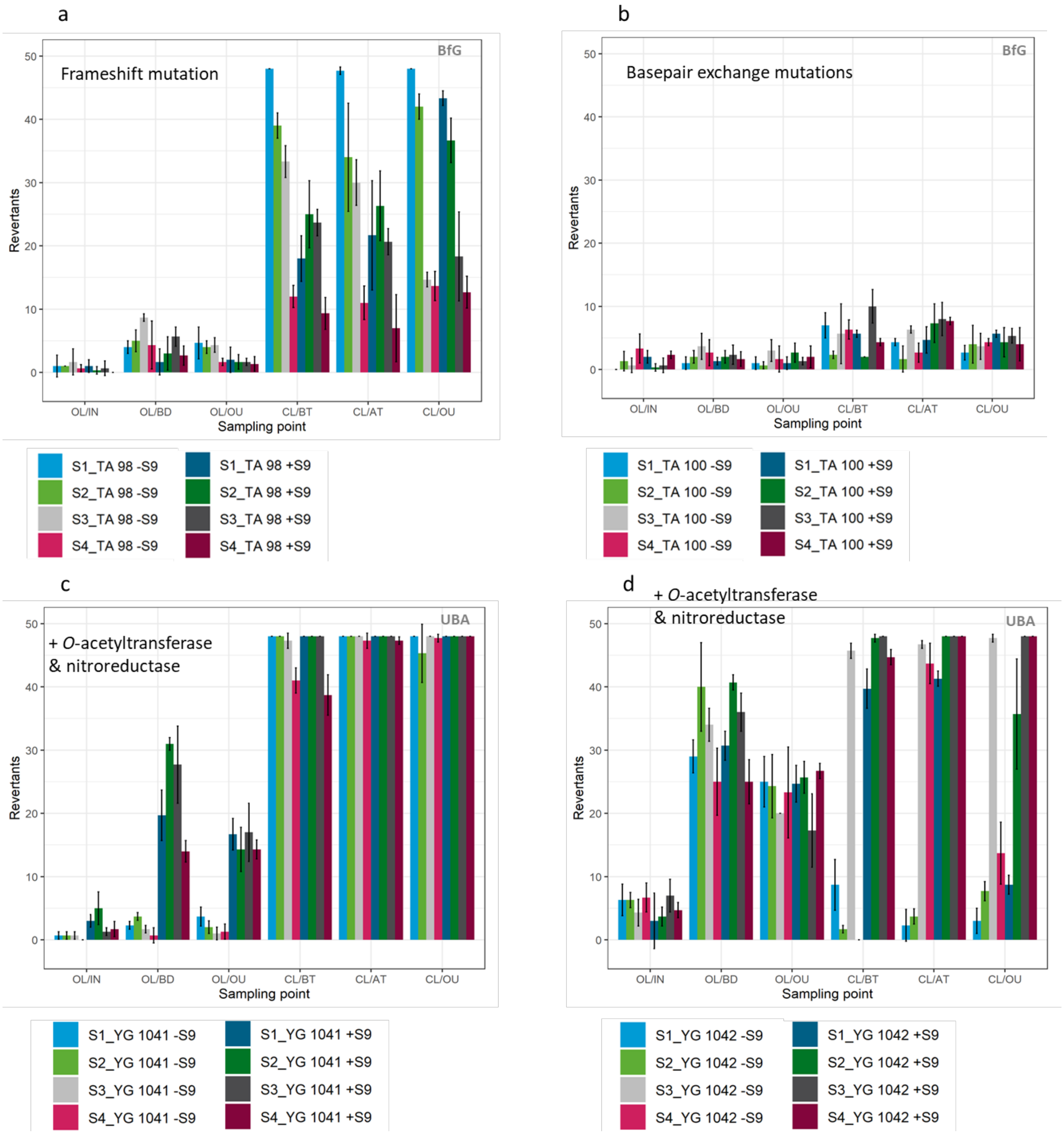
3.6.2.2 Ames mutagenicity test

The results of the Ames tests on undiluted sample extracts (Figure 23) demonstrated mutagenic activity of all CL samples and most OL samples, but no mutagenicity of inlet samples. Overall, the mutagenic potential (in terms of number of revertants) was on average higher in the CL than in the OL samples, although the variation between the ships was large. In particular for the TA98 strain (Figure 23a), indicating frameshift mutation causing compounds, and the point mutation sensitive strain YG1042 (Figure 23d), the variations in the number of revertants in the CL samples were prominent between the ships, ranging from control level values (strain YG1042) to the maximum number of revertants. When comparing the two strains, the differences in the specificities of these strains become obvious. TA98 showed the highest mutagenicity in all CL samples of ships S1 and S2 without metabolic activation by S9 (Figure 23a). Addition of S9, however, decreased the mutagenic potential of the samples CL/BT and CL/AT of all four ships but did not significantly alter the mutagenicity of the CL/OU samples. This may indicate that new mutagenic agents were formed and/or an enrichment of mutagens occurred during storage of the CL discharge which did not need metabolic activation, at least in case of S1 and S2.

In terms of mutagenicity by aromatic amines and nitro compounds, strain YG1042 showed that the CL/BT und CL/AT samples of the ships S1 and S2 obviously contained a significant proportion of pro-mutagens which were activated after the addition of S9. However, there was no effect of S9 in the OU sample of S1 and a less pronounced effect for S2. The CL samples of S3 were an exception because they showed no effect of S9.

OL/BD and OL/OU samples caused moderate point mutation revertant counts in YG1042 (Figure 23c) whereas TA98 (Figure 23a) showed little frameshift mutagenic activity, just above the negative control level. An effect of metabolic activation by S9 was not detectable but a trend to lower revertant counts after dilution in OL was noticeable.

Figure 23: Mutagenicity of scrubber water samples in *Salmonella spp*. mutant strains (Ames fluctuation test)



Number of revertants of the bacterial strains *Salmonella enterica* subsp. *enterica* serotype Typhimurium a. TA98, b. TA100, c. YG1041 and d. YG1042 after exposure to the extracted scrubber water samples at a final concentration factor of 20 (a and b) and 25 (c and d). Shown are the mean values ± standard deviation for n = 3 (technical replicates), 48 wells per replicate. Sampling codes as described in Table 2; here, OL/BD in S4 corresponds to OL/BT.

The strain TA100 showed for all samples no activity of point mutation causing agent (Figure 23b). However, YG1041 (Figure 23c) indicated the presence of pro-mutagenic nitro aromatic compounds and aromatic amines, which caused high revertant counts after enzymatic conversion, in all CL samples. Additional metabolic activation by S9 induced frameshift mutations also in the sample OL/BD and OL/OU. Similar to YG1042, this effect was diminished in the outlet samples due to dilution.

In summary, the findings regarding mutagenicity of the scrubber water samples were:

- Inlet samples were not mutagenic.
- OL samples were less mutagenic than CL samples.
- Most CL samples lead to the highest possible number of revertants in at least one of the four *Salmonella* strains.
- TA98 and TA100 as well as YG1041 and YG1042 differed in their responses with regard to mutagenic activity and metabolic activation.
- Mutagenic effects of OL/BD samples were diminished in the OL/OU samples due to dilution.
- Metabolic activation by S9 enhanced mutagenicity of most samples in the YG strains (except for inlet) but decreased the mutagenic activity in TA98.
- Ships differed in their responses with respect to the used test strains.

3.6.3 Fish-egg toxicity

Fish-egg tests did not provide consistent results that could have been used for an overall evaluation. The test results, not shown in this report, were characterized by variabilities which cannot be explained by plausible reasons and were therefore considered invalid. In order to investigate whether this test is suitable for this type of samples in general, further tests on zebrafish eggs are contracted out.

4 General discussion

4.1 Implications of the chemical composition and ecotoxicity of scrubber discharge water

This and other studies (EGCSA and Euroshore, 2018; Kjølholt et al., 2012; Koski et al., 2017; Magnusson et al., 2018; Schmolke et al., 2020; Ushakov et al., 2019) have shown that scrubber discharge water contains pollutants that are considered persistent, toxic and bioaccumulative such as heavy metals and PAH. For instance, cadmium, lead, mercury, nickel, benzene, naphthalene, anthracene, fluoranthene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*ghi*]perylene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*]pyrene and dioxins, found in scrubber discharge water, are considered priority substances in the context of the EU Water Framework Directive according to Directive 2013/39/EU. These priority substances are identified to pose a significant risk to, or via, the aquatic environment, thus environmental quality standards have been defined as benchmarks for the assessment of good surface water chemical status. According to the Commission Decision (EU) 2017/848, EU Member States should adopt measures to control pollution by these substances also within their coastal and territorial waters under the Marine Strategy Framework Directive (MSFD). Of special concern regarding scrubber discharge water are nickel, lead and PAH, which showed a clear enrichment in the analysed discharge water. In the present study, cadmium and mercury showed an extremely low enrichment potential (see Table 11), while dioxins were not found (<LOQ) in any water sample but in scrubber sludge samples.

The priority label given to the substances above does not imply that other pollutants contained in scrubber discharge water are irrelevant. On the contrary, they contribute to the mixture toxicity. The ecotoxicity testing with marine organisms showed for the majority of the scrubber water samples acute toxic effects which were caused by all contaminants contained in the water samples combined. However, there were remarkable differences in the ecotoxicological effects between OL and CL samples. Discharge waters from CL were classified throughout as extremely toxic and from OL as from practically non-toxic to considerably toxic. However, the OL samples should not be considered harmless. The results of the chemical analysis clearly showed that the OL-discharge water contains pollutants of high concern. The WET tests conducted only reflect acute toxic effects and, as many of the pollutants present in the discharge waters are persistent and bioaccumulative, toxic effects are more likely to increase with longer exposure durations. The OL and CL discharge samples also showed mutagenic potency in at least one of the bacterial strains although overall the OL discharge samples were less mutagenic than the CL discharge samples. Further, dioxin-like effects were detected in CL discharge samples by a hAHR-specific, yeast-cell based bioassay.

As the prominent differences in the ecotoxicological effects between OL and CL samples are concerned, the results of the chemical analysis could not provide any substantial evidence as to what single substance or group of substances may have been a driver of the higher toxicity in the CL samples. The only conspicuously higher concentrations in the CL compared to the OL samples where the high-molecular weight PAH and the metals nickel and vanadium, and for the ships S1 and S3 also copper. The metals nickel and copper are both well known to be highly toxic to aquatic organisms ranging from algae to fish. Vanadium is far less well studied but the results of the existing studies, of which some were performed in the 1960s and 1970s, suggest that the toxicity is not particularly high, reporting acute toxicity thresholds in the mg/l-range, for example, for *Daphnia magna* and zebrafish (*Danio rerio*) (Beusen & Neven, 1987). Also, most studies on aquatic organisms used only pentavalent and no tri- or tetravalent vanadium compounds and thus, the influence of speciation on the toxicity is not known. The National Institute for Public Health and Environment (Smit, 2012) proposed 1.2 µg/l for long-term direct toxicity and 3.0 µg/l for short-term concentration peaks as quality standards for vanadium in freshwater; however, risk limits for saltwater based on direct ecotoxicity could not be derived. The European Chemical Agency (ECHA, n.d.) suggests a predicted no-effect concentration of 2.5 µg/l for vanadium in marine water.

In order to better assess the environmental risks related to the release of scrubber discharge water, realistic and conservative exposure scenarios have to be modelled to determine the distribution and fate of the pollutants from scrubber discharge water.

4.2 Issues related to sampling procedures and monitoring of scrubber discharge water

The conducted sampling campaign within ImpEx also served to observe the real conditions of the scrubber systems on board. Suitable sampling possibilities and reliable monitoring of discharge water are essential for compliance control of the discharge criteria.

In the sampled ships within ImpEx, missing and unsuitable sampling points for some targeted water streams were noticed. In those cases, and when possible, we changed the sampling point fittings to ensure correct sampling. This was expected and understandable for targeted water streams that are not required for compliance control, for example, before water treatment (OL/BT and CL/BT). However, it is alarming when the water stream in question is essential for compliance control. The deficiencies in the sampling points included:

- unsuitable valve diameter,
- corrosive materials (e.g. copper and brass) prone to sample contamination,
- unfavorable position to obtain representative samples (e.g. sampling valve next to an elbow or in a vertical pipeline with flow downwards), and
- poor accessibility to ship personnel.

The previous versions of the 'EGCS Guidelines' did not include any requirement for the sampling points, materials and their position. Only the revised '2021 EGCS Guidelines' include a poor guidance for water sampling points. This means, there is room for improvement from a regulatory point of view to make a better specification for the sampling points, materials and positions.

Another issue found on board, which is related to deficiencies in the regulation, was noted with the discharge of stored bleed-off water from CL operation. Two of the sampled ships did not have any discharge limit specification for CL discharges in their documentation. Consequently, there was no monitoring equipment installed for CL discharge besides a turbidity sensor downstream of the bleed-off treatment unit. We believe that this behavior is a consequence of missing specifications in the regulation. The discharge criteria in the 'EGCS Guidelines' were originally developed for OL systems, as CL systems were not present as maritime application for the removal of SOx from the exhaust gas. Yet, their application on merely CL systems is possible. However, for hybrid systems there is a lack of clarity due to the complexity in the operation of those systems. As a matter of fact, here the CL-discharge water (bleed-off) is mixed with the OL-discharge water because the stored water from CL operation is normally released during OL operation. Thus, the effluents are monitored in the outlet as a mixture and compliance with the discharge criteria is verified considering the limit values applicable to OL discharges. The revised '2021 EGCS Guidelines' addressed that issue and set clear criteria for discharge water from temporary storage (prior to any mixture). However, the new guidelines only apply to new installations.

It was observed that it is practically impossible to obtain the specific flowrate for CL operation in hybrid systems based on the available monitoring data. Hence, we used sulphur concentration of the water samples as an indication of how 'frequent' the bleed-off water was recirculated to obtain the specific flowrate, provided that SFOC and fuel sulphur content are known. Alternatively, the water volume sent to the holding tank after a specific operational period could be recorded and, together with the power consumption data, the specific flowrate could be easily obtained. This is important because this parameter is required to calculate emission factors and to estimate discharge volumes in model scenarios.

Very low pH limit values for discharge water, ranging from 2.4 to 4.0, were observed in the documentation (EGCS Technical Manual) of the sampled ships. Those limit values were determined to ensure a pH value no lower than 6.5 at a distance of 4 m from the overboard discharge point as it is allowed in the 'EGCS Guidelines'. However, within this initial mixing zone the acids can have an adverse acute effect on marine organisms.

In section 3.4, the results of the online monitoring data for discharge water were discussed. There, we corroborated the monitoring issues reported by other studies. It was mentioned that correct installation as well as periodic calibration and maintenance of the measuring equipment are essential for accurate monitoring. In the sampled ships, maintenance is conducted mainly monthly and calibration yearly, except for the pH meter that is calibrated monthly. That periodicity agrees with the recommendation given by a manufacturer (TriOS, n.d.). But, the same manufacturer also recommends weekly cleaning of the equipment; which is important considering the presence of solids and oil residues in the scrubber water streams. Also, in section 3.4 issues related to the measurement of PAH_{phe} are described.

The issues mentioned above impair the correct compliance control. Nevertheless, we consider the topic to have lower priority than the environmental risks derived from the release of scrubber discharge water (even being compliant with the discharge criteria). As stated by Marin-Enriquez et al. (2021), the discharge criteria do not represent any practical restriction for conventional scrubber systems, so that most probably the criteria are fulfilled (except for water from temporary storage in future installations). Therefore, efforts should not be focused in the first place on solving the issues related to water monitoring, but instead on addressing the environmental risks of scrubber discharge water and developing the required regulation to protect the environment.

4.3 Proposal for regulation of scrubber discharge water

A main task within the ImpEx project was the evaluation of existing regulations for scrubber discharge water. Based on the results from the chemical and ecotoxicological analyses, ImpEx aimed at determining whether further regulatory measures are required to ensure the protection of the marine environment. The status quo of the regulatory framework was reported in the previous ImpEx publication (Marin-Enriquez et al., 2021). Since then, two further developments in the regulation were concluded: the revised '2021 EGCS Guidelines' (resolution MEPC.340(77)) and the "Guidelines for risk and impact assessments of the discharge water from EGCS" (circular MEPC.1/Circ.899).

Nine different potential measures and regulation amendments for the discharge water from scrubbers were evaluated. These are based on the recent developments of the scrubber regulation, proposals submitted to the IMO committees, regulatory measures in place for other ship waste streams, preventive actions taken by port and coastal States and discussion work in committees different to IMO.

Table 18 presents the potential measures and the results of their evaluation. The rated effectiveness, the timescale for expected implementation and possible application (on existing fleet/new installations) for every measure are included in the table. It is considered of high relevance that a measure should also apply to existing installations and not only to future ones. For instance, measure 1 “Review of the discharge criteria in the ‘EGCS Guidelines’ (resolution MEPC.340(77))” in Table 18 was evaluated with low effectiveness as it would not apply to existing scrubber-fitted ships, which cover 24.8 % of the dead-weight tonnage of the total fleet of merchant seagoing vessels (see Appendix A). In fact, the share of HFO in the marine fuel market is still significant (~20 % according to Oosthoek, 2021; and around one third according to Netherlands, 2022) because of the current number of ships operating with scrubbers. Considering that the mean lifetime of a ship is 25 to 30 years, it can be expected that the operation of scrubbers will continue as long as it is legally possible and economically reasonable. The gap between the costs of HFO and LSFO (see Appendix A) as well as the existing and future requirements for climate protection are key drivers for scrubber installations on newbuildings.

Regarding regulatory decisions for climate protection, the initial IMO greenhouse gas (GHG) strategy aims to reduce GHG emissions of international shipping and phase them out as soon as possible in this century, and includes the following levels of ambition:

- To review the energy efficiency design requirements for ships to decline carbon intensity (emissions per transport work)
- To reduce by at least 40 % carbon intensity by 2030, pursuing efforts towards 70 % by 2050 compared to 2008 levels
- To peak GHG emissions as soon as possible and to reduce the total annual GHG emissions by at least 50 % by 2050 compared to 2008 levels

Recently, several measures and programs have been initiated by the industry in response to the IMO strategy for GHG reduction. The media report continuously about current developments, for example the use of onshore power on ports, trial voyages using biofuels mixed with distillate fuels and new orders of methanol-ready ships. These first steps are seen as positive developments and are required for the maturity of the market for alternative fuels and technical solutions. Nevertheless, DNV (2022) forecasted an energy share in the range 1 to 8 % for HFO in combination with scrubbers by 2050 for the scenarios based on the decarbonization pathways of the IMO ambitions.

In Table 18, measure 2 is of special attention, which is the “Application of the recently developed risk and impact assessments guidelines for the evaluation of possible harmful effects of discharge water in areas to be assessed (MEPC.1/Circ.899)”. In this measure, States are advised to conduct an environmental risk assessment according to a unified approach when considering local or regional restrictions. This measure did not obtain an evaluation with high effectiveness. The conduction of a risk and impact assessment is time-consuming and costly, which could delay the designation of restrictive areas. Further, this measure does not ensure a global protection as it depends on the initiative of single States to call for restrictions “in their ports, harbours, estuaries, or coastal and other territorial waters” (IMO, 2022). Therefore, we considered additional measures as needed.

The abovementioned guidelines in MEPC.1/Circ.899 (IMO, 2022) state under paragraph 7.4 that "the adoption of restrictions or a ban on discharge water from EGCS should be considered in areas where any of the following indicative criteria are fulfilled:

1. environmental objectives in the areas are not met, e.g. good chemical status, good ecological status or good environmental status are not achieved under applicable legislation;
2. the discharge of EGCS effluents represents an additional risk of deteriorating the environment and the resiliency of the climate system;
3. the EGCS discharge water conflicts with the conventions and regulations formulated to protect the marine environment (see UNCLOS Article 195, etc.); and
4. the EGCS discharge effluent represents an increase in the costs of management of dredged materials in ports."

Regarding point 1, marine waters in the EU are assessed based on the environmental objectives set in the MSFD, which is the applicable legal framework. Looking at the results of the last Good Environmental Status (GES) assessment for the Baltic Sea, a high percentage of the overall status assessment is shown as 'GES not achieved' in almost all reported features (WISE Marine, 2021). Moreover, the results of the report of the second HELCOM holistic assessment (HELCOM, 2018) showed that the environmental objectives of the Baltic Sea Action Plan are not likely to be reached by 2021.

Regarding point 2, several substances contained in scrubber discharge water are identified to pose a significant risk to the aquatic environment (see section 4.1). Concerning the deterioration of the climate system, the ongoing international project ShipTRASE investigates how scrubber discharge water influences the biogeochemical cycling of biogenic trace gases, such as dimethyl sulphate and isoprene, and the air-sea exchange that in turn influence global climate and air quality (Belmont Forum, 2020). Also, the depletion of the water alkalinity in the OL operation and the discharge of acidic water can decrease the ocean's carbon dioxide uptake capacity.

Regarding point 3, FOEI et al. (2022) outlined in the IMO submission MEPC 79/5/3 how the release of scrubber discharge water into the marine environment raises issues of inconsistency with the law of the sea obligations of States to protect and preserve the marine environment.

Measure 3 in Table 18, "Harmonized call for a discharge ban within 12 or 3 nautical miles from the nearest coast", is considered an appropriate measure with possibilities for acceptance in the IMO committees and reasonable implementation time scale. Recent studies have estimated the amount of discharge water in areas close to the coastline. It was estimated that 25 % (Tronczynski et al., 2022), 21 % (Jalkanen et al., 2022) and 18 % (Osipova et al., 2021) of the scrubber discharges in France, in the OSPAR region and worldwide, respectively, occurred within 12 nautical miles of the coastline and in internal waters. Hence, this measure would have a great impact by avoiding the release of pollutants in the determined areas. Since the shipping industry is familiar with restrictions inside the 12-nautical mile zone, the application of this measure seems to be simple and would require to switch to compliant fuel or to CL operation (in 'zero discharge' mode) in the restricted area, which could cause a drawback. In this case, the stored water in the holding tank would probably be discharged close to the borders of the restricted areas, which could increase the risk of creating hotspots. As an accompanying measure, moderate discharge flowrates for stored water could be regulated.

Furthermore, with a view to our national seas, like the Baltic Sea, we should also urgently discuss the measure 4 (Table 18) "Harmonized call for discharge ban in specific areas such as Particularly Sensitive Sea Areas (PSSA) and Special Areas" whether and how an implementation could be realized. The Baltic Sea is currently considered to be one of the most polluted sea areas in the world (HELCOM, 2010) and therefore, it needs great efforts for its protection. In the case of a discharge ban in the Baltic Sea Region, it could be still possible to fully operate in CL mode, especially in ferry operations, and to deliver the discharge water into port reception facilities accordingly, as long as the storage capacities on board and the infrastructure at ports make it possible. Certainly, discussion and progress regarding this issue at IMO level would be a worthwhile aim. However, due to the regional nature of the matter, it would be advisable to move it forward also at the Baltic Marine Environment Protection Commission (HELCOM) level. Actually, the updated Baltic Sea Action Plan (HELCOM, 2021), which is HELCOM's strategic programme of measures and actions for achieving a GES of the sea, includes a scrubber-related action to develop a roadmap by 2025. The aim is to reduce the input of pollutants from scrubber discharge waters, as a minimum in line with existing legislation, taking into consideration the precautionary principle and the outcome of the IMO work. Similarly, under the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR), the Environmental Impacts of Human Activities Committee agreed in its last meeting to develop protective measures with regard to scrubber discharge water.

There is a clear chance to bring new measures into discussion within the IMO. The output on "Evaluation and harmonization of rules and guidance on the discharge of discharge water from EGCS into the aquatic environment, including conditions and areas" is not yet concluded and the task on the development of regulatory matters are still pending. The 77th session of the MEPC resolved to resume that work after PPR 10 and to extend the target completion year to 2025.

Table 18: Potential measures and regulation amendments for the discharge water of scrubbers

Measure	Rationale	Benefits	Penalties	Evaluation and effectiveness
1 - Review of the discharge criteria in the 'EGCS Guidelines' (resolution MEPC.340(77))	Current discharge criteria were defined without sufficient studies on the composition of discharge water and its environmental effects. They are focused only on the prevention of acute effects and include a clause for the review in the future as more data become available. The current discharge criteria do not pose sufficient protection for the marine environment in the long term (accumulation effects) and do not imply any practical restrictions for OL-discharges (no water treatment is required). The discharge criteria could be reviewed to contain stricter limits and to include additional parameters such as heavy metals. The latter requires frequent sampling and measurement in the laboratory, as online monitoring is not possible.	<u>Marine environment.</u> Reduction of pollutant loads (e.g. heavy metals) to the sea.	<u>Industry.</u> New scrubber systems would have presumably stricter criteria than older systems. Thus, they are expected to be more expensive (investment and operation) due to the requirement of more efficient water treatment. Moreover, it may imply additional labour activities for the crew.	**Effectiveness: low** Implementability: in >5 years Application: new installations This measure could make scrubbers economically less attractive, consequently, new installations can decrease or even stop. In the future, less scrubber installations are expected anyway due to coming IMO regulations on climate protection and changes in the fuel market (i.e. introduction of alternative fuels). Due to the grandfather clause, the reviewed guidelines would apply only to new installations. Consequently, the existing ships with scrubbers will continue discharging water fulfilling only the current discharge criteria.
2 - Application of the recently developed 'risk and impact assessments guidelines' for the evaluation of possible harmful effects of discharge water in areas to be assessed	Many coastal and port States have already declared local discharge bans/restrictions. Those decisions are usually taken unilaterally and based on their own rationale. With this measure, the designation of areas with discharge ban/restrictions should be based on the results of environmental risk	<u>Marine environment.</u> Areas with high environmental risk due to the release of scrubber discharge water can be protected. <u>Regulatory framework.</u>	<u>Industry.</u> In areas with designated bans/restrictions alternative solutions would be needed (e.g. use of compliant fuels, operation of CL in 'zero discharge' mode) which are more costly. Also, depending on the extension of the areas with a discharge ban, port reception facilities could be made	**Effectiveness: moderate** Implementability: immediately (as the risk and impact assessments can be initiated any time, however additional time should be considered to conclude the risk and impact assessments and for designation procedures) Application: all systems

Measure	Rationale	Benefits	Penalties	Evaluation and effectiveness
(MEPC.1/Circ.899)	and impact assessments conducted following agreed guidelines.	Harmonized and consistent procedures/rationale for designation of restrictions.	available for disposal of stored water (in case of CL operation in 'zero discharge' and not enough storage capacity on board). Moreover, vessel management should keep information updated about existent areas with a ban/restriction. Marine environment. When using CL in 'zero discharge' mode, the stored water in holding tank would potentially be discharged in areas close to the borders of the restricted areas.	The conduction of a risk assessment is time-consuming and costly. Moreover, many of the States with concerns about scrubber discharges have already set bans/restrictions.
3 - Harmonized call for a discharge ban within 12 or 3 nautical miles from the nearest land (as amendment in Annex VI or new MEPC resolution)	Generally, coastal waters are more vulnerable and at the same time more polluted. Coastal waters therefore require more protection than the open ocean, which has a better resilience capacity. This measure is also applied for other waste streams from ships (e.g. garbage and sewage).	Marine environment. Coastal waters can be protected. Regulatory framework. Relatively clear regulation easy to understand and to be monitored.	Industry. Alternative solutions are needed (e.g. use of compliant fuels, operation of CL in 'zero discharge' mode) which are more costly. Moreover, it may imply additional labour activities for the crew. Marine environment. When using CL in 'zero discharge' mode, the stored water in holding tank would potentially be discharged in areas close to the borders of the restricted areas.	**Effectiveness: high** Implementability: in >2 years Application: all systems There is currently no active discussion about this measure. However, some countries (PPR 7/12/1) called for consideration of this measure for the discussion within the output on "Evaluation and harmonization of rules and guidance on the discharge of discharge water from EGCS into the aquatic environment, including conditions and areas".
4 - Harmonized call for discharge ban in	Specific areas such as enclosed or semi-enclosed water bodies require	Marine environment. Specific vulnerable	Industry. Alternative solutions are needed (e.g. use of	**Effectiveness: high** Implementability: in >2 years

Measure	Rationale	Benefits	Penalties	Evaluation and effectiveness
specific areas such as PSSA and Special Areas (as amendment in Annex VI or MEPC resolution)	special protection. This measure is applied for other waste streams from ships (e.g. garbage and bilge water).	areas can be protected. <u>Regulatory framework.</u> Relatively clear and easy regulation to understand and monitor.	compliant fuels, operation of CL in 'zero discharge' mode) which are more costly. Moreover, it may imply additional labour activities for the crew. Also, depending on the extension of the areas with a discharge ban, port reception facilities could be made available for disposal of stored water (in case of CL operation in 'zero discharge' and not enough storage capacity on board). <u>Marine environment.</u> When using CL in 'zero discharge' mode, the stored water in holding tank would potentially be discharged in areas close to the borders of the restricted areas.	Application: all systems There is currently no active discussion about this measure. However, ICES (MEPC 76/6/9 and MEPC 76/INF.5), FOEI, Greenpeace International, WWF, Pacific Environment and CSC (MEPC 76/9/8) called for consideration of this measure for the discussion within the output on "Evaluation and harmonization of rules and guidance on the discharge of discharge water from EGCS into the aquatic environment, including conditions and areas".
5 - Mandatory carriage of sufficient compliant fuel despite use of scrubber on board (amendment of MARPOL Annex VI and/or MEPC.1/Circ.883)	Carriage of compliant fuel on ships with scrubbers for its use in case of scrubber-failure was discussed during the review of MEPC.1/Circ.883/Rev.1 at MEPC 77. Making the carriage of sufficient compliant fuel mandatory would indirectly make the installation and operation of scrubber unattractive.	<u>Marine environment.</u> Global marine protection due to indirect phase-out of scrubber technology.	<u>Industry.</u> 'Voluntary' stop or decrease on the use of scrubber is costly. <u>Regulatory framework.</u> Additional aspect to be controlled during PSC.	**Effectiveness: low** Implementability: in >2 years Application: all systems There is currently no active discussion about this measure. MEPC.1/Circ.883 was recently reviewed (MEPC 77) and no concerns or intentions for a further review was envisaged. It is challenging to get a consensus to adopt this measure. Moreover, there is no guarantee of an indirect phase-out of EGCS.

Measure	Rationale	Benefits	Penalties	Evaluation and effectiveness
6 - Phasing-out of future installations: EGCS not accepted as equivalent method anymore (as amendment in Annex VI or MEPC resolution)	The equivalency of scrubber as alternative to compliant fuel is put into question due to the environmental concerns about water discharges and risks of HFO spillage.	Marine environment. Partial protection to the marine environment. Risks related to HFO carriage are partly resolved.		**Effectiveness: low** Implementability: in >3 years Application: new vessels There is currently no active discussion about this measure. Future installations are prevented. The existing ships with scrubbers will continue discharging water. The rejection of scrubber as equivalent method seems to be extremely unlikely because it implies the refusal of an existing regulation. However, FOEI, Greenpeace International, WWF, Pacific Environment and CSC (MEPC 79/5/3) outlined that the use of scrubbers as an alternative compliance mechanism, with the consequential discharges, raises concerns over inconsistencies with the law of the sea obligations.
7 - Phasing-out of scrubber operation or global discharge ban (as amendment in Annex VI or MEPC resolution)	The share of HFO in the marine fuel market is still significant (~20 %) because of the current number of ships with scrubbers. Mean lifetime of ships is 25-30 years; thus, operation of scrubber in the long term is expected as long as the regulations stay unmodified.	Marine environment. Global protection to the marine environment. Risks related to HFO carriage are partly resolved.	Industry. Economic consequences due to the shift to compliant fuels. However, return of investment of the scrubber is expected to be reached until the possible implementation of this measure.	**Effectiveness: high** Implementability: in >3 years Application: all systems Future water discharges are prevented in the long term. There is no current active discussion about this measure. However, ICES (MEPC 76/6/9 and MEPC 76/INF.5), FOEI, Greenpeace International, WWF, Pacific Environment and CSC (MEPC 76/9/8) called for consideration of this measure for the discussion within the output on "Evaluation and harmonization of rules and guidance on the discharge of discharge water from EGCS into the

Measure	Rationale	Benefits	Penalties	Evaluation and effectiveness
				aquatic environment, including conditions and areas".
8 - Set a global ban on the use of HFO (as amendment in Annex VI or MEPC resolution)	HFO spillages are environmental disasters. Use of HFO does not align itself with the efforts for climate neutrality.	Marine environment. Global protection to the marine environment. Risks related to HFO carriage are partly resolved.	Industry. Economic consequences due to the shift to compliant fuels. However, return of investment of the scrubber is expected to be reached until the possible implementation of this measure.	**Effectiveness: moderate** Implementability: in >5 years Application: all ships There is a ban on the use of HFO in the Arctic and Antarctic. A global ban could follow as an extension but is currently not actively discussed.
9 - Local discharge bans (ports and territorial waters) declared by port and coastal States without following specific globally agreed guidelines (MEPC.1/Circ.899)	Based on their own judgement and/or by applying domestic regulations, port and member States can declare local discharge ban/restrictions as necessary in areas under its jurisdiction. Ports receive already a high input of contaminants from different sectors (in addition to shipping).	Marine environment. Quickest measure to protect local waters.	Industry. In those areas alternative solutions are needed (e.g. use of compliant fuels, operation of CL in 'zero discharge' mode) which are more costly. Moreover, vessel management should keep information updated about existent ban/restrictions.	**Effectiveness: moderate** Implementability: immediately Application: all systems It has been a measure adopted by many countries before the 'Guidelines on risk and impact assessments' (MEPC.1/Circ.899) were adopted.

Implementability refers to the estimated time required to the measure to take effect considering its current state (e.g. not active current discussion, under discussion and already approved) as starting point.

5 Conclusion and outlook

The information gained in the present study in combination with data from other studies and realistic exposure scenarios allows for a more accurate assessment of the environmental risks related to the release of scrubber discharge water into the marine environment. The ongoing project MOSAB, which is being carried out by BSH on behalf of UBA, deals with modelling of the distribution of discharge water and pollutants from scrubber in the marine environment, especially in the North Sea and Baltic Sea.

ImpEx and other studies showed that OL scrubber discharge water is clearly of high concern for the marine environment. Despite the efficiency of water treatment units in CL operation, ecotoxicological analyses indicated extremely high toxicity for CL discharge water, hence its discharge into the marine environment is not an option. In conclusion, the present results and also other studies indicate that there are potential detrimental effects for marine ecosystems from scrubber discharge water.

Another not yet so well-known problem with scrubber discharge water is that it can even cause more radiation through effects on the marine biology that may lead to a facilitation of global warming (Booge and Marandino, 2022).

The current IMO regulation for scrubber discharge water was assessed as insufficient to ensure the necessary protection for the marine environment. The ‘2021 EGCS Guidelines’ (resolution MEPC.340(77)), which were developed considering only the prevention of acute effects, do not provide sufficient protection for the marine environment in the long term. This is of concern as these guidelines allow for the release of persistent, bioaccumulative and toxic substances. In addition, the ‘2021 EGCS Guidelines’ need improvement in terms of sampling procedures and online monitoring requirements. However, we consider it more efficient to focus efforts on developing further protective measures rather than a revision of these guidelines. The recently adopted “Guidelines for risk and impact assessments of the discharge water from EGCS” (circular MEPC.1/Circ.899) advise to conduct an environmental risk assessment according to a unified approach when considering local or regional restrictions. This measure was evaluated as moderately effective, mainly because conducting risk and impact assessments is time-consuming and costly, which could delay the designation of restrictive areas. In addition, it only allows a ban in territorial waters, which is not an effective measure in the case of the highly impacted Baltic Sea, for example, and can only be seen as a first step (see also below).

The market analysis showed that about 25 % of the global merchant fleet (by dead-weight tonnage) is equipped with a scrubber system, which is reflected in the still significant share of HFO in the marine fuel market. The use of HFO in combination with scrubbers is expected in the long term, even by 2050. In consideration of this, we strongly recommend that additional protective measures are taken immediately as needed. The “Harmonized call for a discharge ban within 12 or 3 nautical miles from the nearest coast” is considered an appropriate measure with a high protective effect as well as a reasonable timeframe for implementation.

Further, the measure “Harmonized call for discharge ban in specific areas such as PSSA and Special Areas” should also be considered urgently, especially with regard to the Baltic Sea as this is currently considered to be one of the most polluted sea areas in the world (HELCOM 2010a). Therefore, any further avoidable pollution by scrubber discharge water should be stopped immediately or at least at the earliest possibility. The Baltic Sea has very low resilience and compensatory capacity in its current state. Action should also be taken as quickly as possible at HELCOM level.

Furthermore, a well-founded assessment of the paper by FOEI et al. (2022) (MEPC 79/5/3) would be desirable. The question raised here about the incompatibility with the obligations of States under the law of the sea (UNCLOS) to protect and conserve the marine environment should be answered by the relevant bodies.

Further studies and models can help to better understand effects in the marine environment, however, it is recommended to protect sensitive or highly polluted areas (e.g. Baltic Sea) from discharges as soon as possible.

It can be concluded that the discussion on protective measures with regard to scrubber discharges needs to be urgently addressed in all relevant committees, such as IMO, OSPAR and HELCOM, as well as at the general EU, the regional and the national level. Finally, the global use of scrubbers is questionable even as a transitional technology. Specially, in view of climate protection, rather than continuing to use fossil fuels by all means, alternative fuels should be pushed forward.

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A Appendix – Updated scrubber market analysis

The publication “Environmental Impacts of Exhaust Gas Cleaning Systems for Reduction of SOx on Ships – Analysis of status quo” (Marin-Enriquez et al., 2021), compiled within the framework of the project ImpEx, presented a scrubber market analysis as of November 2020. The following tables and figures provide updated information based on the information of the GISIS database from the IMO as of 1 September 2022. A total of 3731 ships with scrubber system are reported. This represents 3.6 % of the global fleet by number of ships (but 20.8 % by dead-weight tonnage). Scrubber-fitted ships cover 24.8 % of the dead-weight tonnage of the total fleet of merchant seagoing vessels.

Panama, Marshall and Liberia (the three biggest flags) are the flags with more scrubber-fitted ships, covering about 50 % of all scrubber installations (see Table A-1).

There was a boom in scrubber installations between mid-2019 and end of 2020, reaching a peak with 351 notifications in December 2019. The average monthly notifications in the first half of 2022 was 30 (see Figure A-1). The current cost gap between high-sulphur and low-sulphur fuel oils is around 250 USD per ton (Ship&Bunker, 2022), which makes the installation and operation of scrubbers very attractive from an economic point of view. The price of distillate fuel (MGO) is currently over 600 USD per ton more expensive than high-sulphur fuel (Ship&Bunker, 2022). For this reason, new scrubber installations are expected to keep at the same rate or even to grow in the coming years, despite the current impetus from alternative fuels.

The market share by type of scrubber and ship type did not show significant changes compared to the former market analysis conducted within this project (Marin-Enriquez et al., 2021). Open loop remains the preferred solution with 86.1 % of the scrubber market, followed by hybrid systems with 13.2 % (see Figure A-2). Bulk carrier, oil/chemical tanker and container ship are the ship types that dominate the scrubber market (see Figure A-3).

Table A-1: Notifications in GISIS about ships scrubber-fitted

Flag State	Notifications [i.]		Total fleet [ii.]		Portion of fleet scrubber-fitted
	Amount	%	Amount	%	
Antigua and Barbuda	8	0.2 %	638	0.6 %	1.3 %
Bahamas	95	2.5 %	1 307	1.3 %	7.1 %
Belgium	8	0.2 %	199	0.2 %	3.5 %
Bermuda (United Kingdom)	23	0.6 %	135	0.1 %	17.0 %
Canada	11	0.3 %	689	0.7 %	1.6 %
Cayman Islands (United Kingdom)	24	0.6 %	139	0.1 %	16.5 %
Cyprus	63	1.7 %	1 030	1.0 %	6.1 %
Denmark	103	2.8 %	731	0.7 %	13.7 %
Finland	26	0.7 %	278	0.3 %	9.4 %
France	12	0.3 %	549	0.5 %	2.2 %
Germany	20	0.5 %	592	0.6 %	3.4 %
Gibraltar (United Kingdom)	1	0.0 %	155	0.2 %	1.3 %
Greece	126	3.4 %	1 234	1.2 %	7.3 %

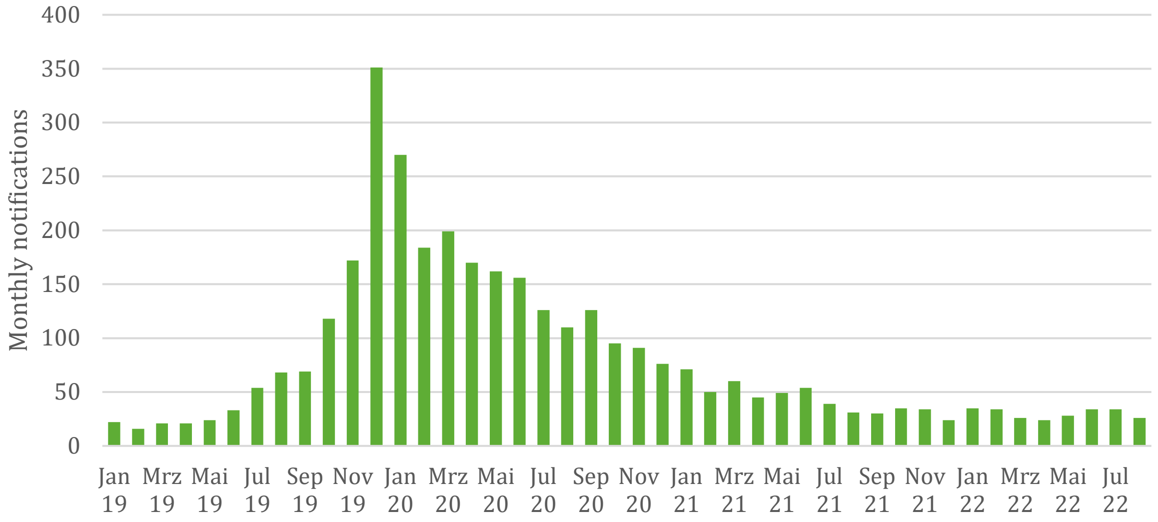
Flag State	**Notifications** [i.]		**Total fleet** [ii.]		**Portion of fleet scrubber-fitted**
	Amount	**%**	**Amount**	**%**	
Hong Kong (China)	234	6.3 %	2 661	2.6 %	4.0 %
India	8	0.2 %	1 810	1.8 %	17.0 %
Isle of Man (United Kingdom)	41	1.1 %	291	0.3 %	1.6 %
Italy	38	1.0 %	1 266	1.2 %	17.3 %
Japan	82	2.2 %	5 590	5.4 %	6.1 %
Liberia	579	15.5 %	4 311	4.2 %	14.1 %
Lithuania	5	0.1 %	62	0.1 %	9.4 %
Malaysia	3	0.1 %	1 790	1.7 %	2.2 %
Malta	259	6.9 %	2 047	2.0 %	3.4 %
Marshall Islands	714	19.1 %	4 042	3.9 %	0.6 %
Netherlands	78	2.1 %	1 175	1.1 %	10.2 %
Norway	48	1.3 %	1 710	1.7 %	8.8 %
Panama	602	16.1 %	8 025	7.8 %	0.4 %
Portugal	65	1.7 %	820	0.8 %	14.1 %
Republic of Korea	28	0.8 %	2 063	2.0 %	3.0 %
Saudi Arabia	2	0.1 %	413	0.4 %	1.5 %
Singapore	255	6.8 %	3 227	3.1 %	13.4 %
Spain	0	0.0 %	2 047	2.0 %	8.1 %
Sweden	10	0.3 %	368	0.4 %	0.2 %
Turkey	29	0.8 %	1 237	1.2 %	12.7 %
United Kingdom	116	3.1 %	1 174	1.1 %	17.7 %
United States	13	0.3 %	3 638	3.5 %	6.6 %
Total amount	**3 729**	**100 %**	**57 443**	**55.8 %**	**3.6 %**

Source: Raw information obtained from GISIS (IMO, 2022) as of 1 September 2022: 3729 ships (notifications).

i. Every notification represents a ship scrubber-fitted already approved.

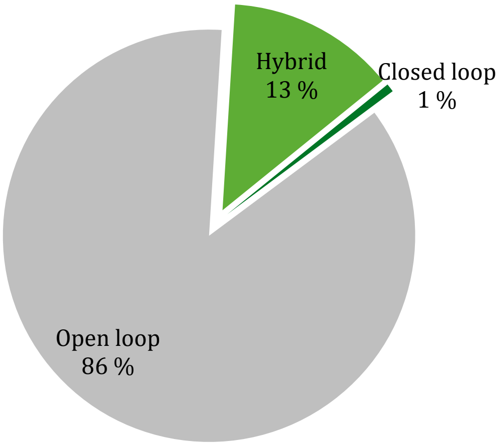
ii. UNCTAD (2022) reports 102 899 propelled seagoing merchant vessels of 100 GT and above in 2022.

Figure A-1: Monthly notifications about ships scrubber-fitted from Jan 2019 to Aug 2022



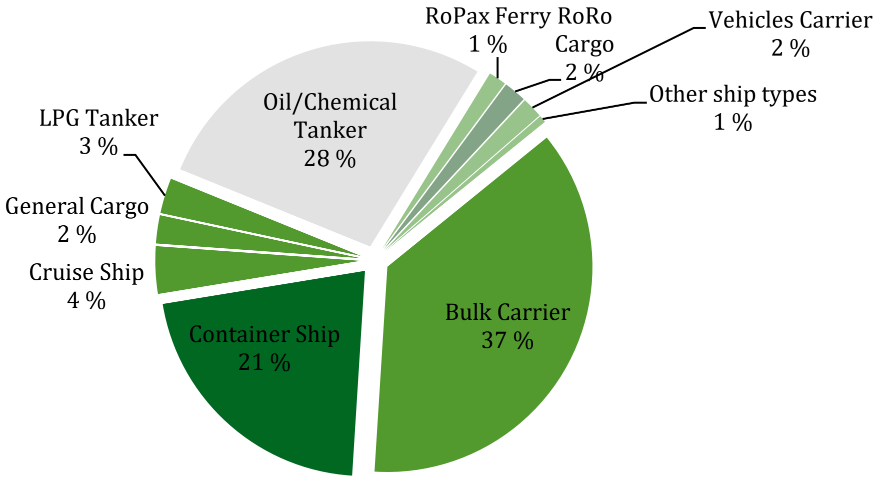
Source: Raw information obtained from GISIS (IMO, 2022) as of 1 September 2022: 3729 ships.

Figure A-2: Scrubber market share by type of scrubber



Source: Raw information obtained from GISIS (IMO, 2022) as of 1 September 2022: 3729 ships.

Figure A-3: Scrubber market share by ship type



Source: Raw information obtained from GISIS (IMO, 2022) as of 1 September 2022: 3729 ships.

B Appendix – Determination of dioxins in scrubber sludge

Scrubber sludge was sampled during the same measuring campaign onboard the ships S2 to S4 (from CL) and onboard ship S3 (from OL). The sludge samples were analysed for determination of dioxin and dioxin-like compounds (in dry matter). The analyses were conducted by the laboratory Umwelt Control Labor GmbH and included polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs). These results, including concentration of suspended solids, are presented in Table A-2.

Table A-2: Dioxin and dioxin-like compounds in scrubber sludge

Parameter	Unit	S2/CL/SL	S3/CL/SL	S3/OL/SL	S4/CL/SL
1,2,3,4,6,7,8- Heptachlorodibenzo-p-dioxin	ng/kg DM	63	810	7.0	70
1,2,3,4,6,7,8-Heptachlorodibenzofuran	ng/kg DM	200	36	<5.0	53
1,2,3,4,7,8,9-Heptachlorodibenzofuran	ng/kg DM	19	19	<5.0	8
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	ng/kg DM	7	37	<3.0	7
1,2,3,4,7,8-Hexachlorodibenzofuran	ng/kg DM	110	57	<3.0	22
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	ng/kg DM	13	170	<3.0	18
1,2,3,6,7,8-Hexachlorodibenzofuran	ng/kg DM	43	22	<3.0	21
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	ng/kg DM	9	130	<3.0	11
1,2,3,7,8,9-Hexachlorodibenzofuran	ng/kg DM	<3.0	<3.0	<3.0	<5.0
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	ng/kg DM	8	41	<2.0	8
1,2,3,7,8-Pentachlorodibenzofuran	ng/kg DM	44	36	<2.0	17
2,3,4,6,7,8-Hexachlorodibenzofuran	ng/kg DM	10	8	<3.0	17
2,3,4,7,8-Pentachlorodibenzofuran	ng/kg DM	16	18	<2.0	22
2,3,7,8-Tetrachlorodibenzo-p-dioxin	ng/kg DM	2	<1.5	<1.0	<1.0
2,3,7,8-Tetrachlorodibenzofuran	ng/kg DM	85	20	<1.0	11
Octachlorodibenzodioxin	ng/kg DM	240	860	25	130
Octachlorodibenzofuran	ng/kg DM	250	160	<10	27
TEQ-Nato/CCMS min [i.]	ng/kg DM	**46.9**	**85.2**	**0.095**	**28.0**
TEQ-Nato/CCMS max [i.]	ng/kg DM	**47.2**	**87.0**	**5.5**	**29.5**
Total suspended solids	mg/l	61000	5900	-	35000

Abbreviations: CL, closed loop; DM, dry matter; OL, open loop; S2-S4, sampled ship; SL, sludge.

i. The toxicity of dioxins is calculated and summed up on the basis of the contents of the individual compounds and their respective factor, and then expressed as a so-called toxic equivalent (TEQ). The TEQ value corresponds to the toxicity of a comparable mass of 2,3,7,8 TCDD. The most common reference framework applied in environmental law to derive an I-TEQ (International-TEQ) is the 1988 I-TEF List by NATO/CCMS (UBA, 2010).

C Appendix – Supplement A: Sampling and analysis protocol within ImpEx campaign

“Supplement A: Sampling and analysis protocol within ImpEx campaign” (version 2.0) provides the procedures for sampling and analysis of water from scrubber as well as fuel and lubricating oil as it was carried out within the ImpEx project. The purpose of the protocol is to preserve quality assurance and quality control, ensure reproducibility within the sampling and analysis campaign and prevent possible uncertainties. The document was provided in advance to the ship operators as well as ship agencies collaborating in the ImpEx project. The protocol is made publicly available on the website of the BSH to ensure transparency and comparability with different data sets.

The document can be downloaded with the following link:
https://www.bsh.de/DE/THEMEN/Forschung_und_Entwicklung/Abgeschlossene-Projekte/_Anlagen/Downloads/sicherheit-und-umweltschutz/ImpEx_final_report_supplement_A.html