Evaluation, control and Mitigation of the EnviRonmental impacts of shippinG Emissions (EMERGE)

EMERGE

Deliverable 2.1,

Database and analysis on waste stream pollutant concentrations, and emission factors¨

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ABBREVIATIONS

BONUS	Funding Agency for Baltic Sea research
BTEX	Benzene, Toluene, Ethylbenzenes and Xylenes
BWMS	Ballast Water Management Systems
CL	Closed loop
DAPSI(W)R(M)	Drivers, Activities, Pressures, State, Impact (on human Welfare), Responses (of Measures)
DIPSIR	Drivers, Pressures, State, Impact and Response
DNV-GL	Det Norske Veritas (Norway)- Germanischer Lloyd (Germany)
EGCSs	Exhaust Gas Cleaning Systems
EPA 16 PAH	16 PAHs issued by the US-EPA
IMO	International Maritime Organization
HCB	Hexachlorobenzene
HNLC	High Nutrient Low Chlorophyll
LOD	Limit of Detection
LOQ	Limit of Quantification

MCR	Maximum Continuous Rating
MEPC	Marine Environment Protection Committee
NO_X	Nitrogen Oxides
OL	Open loop
PAH	Polycyclic Aromatic Compound
RoPax	Vessel that transport cargo and passengers
SHEBA	Sustainable Shipping and Environment of the Baltic Sea region
SO_X	Sulphur Oxides
SPM	Suspended Particulate Matter
THC	Total Hydrocarbon
US-EPA	United States Environmental Protection Agency

EXECUTIVE SUMMARY

From 1 January 2020, the International Maritime Organization (IMO) reduced the maximum allowed sulphur content in ships' emissions from combustion of fuel from 3.5% to 0.5%. To comply with the new regulations, without changing the fuel, many shipping companies have installed exhaust gas cleaning systems (EGCSs) on their vessels. The most common types of EGCS are wet scrubbers; either open loop scrubbers, where seawater is used as cleaning agent of exhaust gases, and the process water is discharged back into the ocean, or closed loop scrubbers, which normally use freshwater for cleaning. In closed systems, a base is introduced to ensure an efficient sulphur oxides (SO_X) uptake. There are also hybrid systems that can switch between open and closed mode. Both operation modes involve discharge of process water, containing a vast number of contaminants and other stressors to the marine environment. The contaminants consist of both metals and organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), that are toxic to marine organisms. Acidifying compounds, formed when SO_X in the exhausts is dissolved during the scrubber process, can reduce the surface water pH and affect the mobility and bioavailability of the co-eluted contaminants. The formation and dissolution of nitrogen oxides (NO_x) presents an additional pressure on the marine environment where the scrubber discharge water contributes to eutrophication, which in turn may lead to an increased oxygen demand in seawater and sediments. The simultaneous release of acidifying compounds, contaminants and nutrients will add pressure to an already exposed environment and the effects are still unknown.

Shipping also emits contaminants and nutrients from other waste streams, including grey water, sewage, bilge water, ballast water and antifouling paints. Hence, although the focus of the EMERGE project is on discharge water from scrubbers, to comprehensively assess the impact of shipping on the marine environment one also need to consider the cumulative pressure from the other waste streams. Therefore, the aim of this report was to summarize and update emission factors from open and closed loop scrubbers, antifouling paints, ballast water, grey water, sewage and bilge water. The pressure categories include contaminants, nutrients and acidifying compounds.

The aim of this report, including a compiled data base (Supplementary Info D.2.1.WasteStreams.xlsx), is to improve the general knowledge of discharges associated with ship induced waste streams; focusing on but not limited to scrubber discharge water. This will further provide support when analysing old and new results and help in the planning of future sampling campaigns.

1 Introduction

Shipping affects the marine environment in different ways via waste streams such as scrubber water, grey water, sewage, bilge water, ballast water and food waste, and indirect via deposition of atmospheric pollutants. Together these sources contain contaminants, nutrients and/or acidifying substances. There is also leakage of contaminants from antifouling paints from ship hulls, spread of invasive species from hulls or ballast water and finally, underwater noise (Figure 1). To be able to assess how shipping activities affect the marine environment, one needs to consider both the cumulative pressure of all waste streams, as well as consider the environmental status of the recipient. The focus of the EMERGE project is however on scrubbers and the impacts it may have on the marine environment.

Scrubbers are used on ships as exhaust gas cleaning systems (EGCSs), primarily to remove sulphur oxides (SO_X) from the exhaust gases to comply to the 2020 Sulphur cap decided by the International Maritime Organisation (IMO) (MARPOL Annex VI Reg.14, 2016). Wet scrubbers (scrubbers from now on), where the exhausts are led through a fine spray of water, are the most common types of EGCS on ships. As of 2020, there are just above 4200 ships being equipped with scrubbers (DNV GL 2020). Once in contact with water, SO_X are readily dissolved, forming sulphuric acid through hydration and oxidation reactions exemplified in Equation *1* (Karle and Turner 2007). Sulphuric acid is a strong acid that will further dissociate, contributing to acidification.

Equation 1 $$SO_X + H_2O + iO_2 \rightleftarrows H_2SO_4 \rightleftarrows SO_4^{2-} + 2H^+$$

SO_X can be both sulphur dioxide (SO_2) and sulphur trioxide (SO_3) and the number of oxygen molecules (*i*) is 0 or 0.5, depending on the number of oxygens in SO_X. This process implies release of two proton (H^+) ions per SO_X molecule, resulting in production of acidic solutions. To maintain the removal efficiency, i.e. the uptake of SO_X, the buffer capacity of the water must be considered. The buffer capacity, i.e. alkalinity, of the water is determined by the excess base that can accept H^+ and neutralise the acidity. The buffering consumes H^+, driving the reaction (Equation *1*) and promotes further dissolution of SO_X.

There are two types of scrubbers; the closed loop type and the open loop type, in addition to a hybrid type where the scrubber can be operated in both modes. According to the latest statistics from DNV GL, 81% of the installed scrubbers are open loop, 17% are the hybrid type and only 1.5% of the share are closed loop scrubbers (DNV GL 2020). In open loop mode, seawater is used as the water source and the natural alkalinity helps buffer the acid addition and the water flow will largely determine the uptake efficiency of SO_X. During open loop mode, large volumes of acidified seawater (~pH 3) (Ülpre and Eames 2014), are produced and discharged to the marine environment. In closed loop mode, freshwater is typically used, recirculated and mixed with a strong base, often NaOH, to increase the waters' alkalinity and the scrubbing efficiency. Since the water is recirculated, much less water is being discharged to the environment, but the discharge water might contain higher concentration of contaminants. In the literature the discharge water is sometime also referred to as "*effluent water", "washwater" or "scrubber water"*. However, in this report we will use the term discharge water.

Apart from SO_X, many other compounds from the fuel, lubricating oils, pipes and combustion engine are washed out in the scrubber. The suspended compounds, e.g. polycyclic aromatic hydrocarbons (PAHs), metals and nitrate, are often partitioned between the dissolved and the particulate fraction, adsorbing to soot and precipitates in the discharge water. The discharge water is not only acidic, it contains a cocktail of different contaminants and nutrients and may therefore add to marine acidification, marine ecotoxicity and marine eutrophication.

The aim of this deliverable is to summarize data on volumes of compounds within each of the three pressure categories contaminants (e.g. PAH and metals), nutrients (nitrogen species) and acidifying compounds (H^+), released from open – and closed loop scrubbers to the marine environment. Emission factors for these scrubber related compounds (discharge rates related to engine power, mg/MWh) are updated.

2 Background

Shipping causes multiple pressure on the marine environment and it is thus important that any assessment of environmental impacts maintains a system's approach. The DPSIR (*Drivers, Pressures, State, Impact* and *Response*) framework is a structured theoretical framework aiming to analyse environmental problems and to identify and propose adequate measures to reduce the problem as such (Atkins et al. 2011; Borja et al. 2006; Relvas and Miranda 2018). DPSIR starts with identifying the driving force (***D****rivers*) that causes specific environmental pressures. The ***P****ressure* on the environment can in turn change the ***State*** of the environment. This change in State may cause an ***I****mpact* on ecosystems and human health as well as the way humans can use the ecosystem (i.e. ecosystem services). Society can then act in different ways to reduce the Pressure by the specific Driver. The latter is termed ***R****esponse*. In a recent study by Elliott et al. (2017) the DPSIR framework was proposed to be extended to DAPSI(W)R(M) in which ***D****rivers* of basic human needs require different ***A****ctivities* which leads to environmental ***P****ressures*. The pressures will lead to a change in environmental ***S****tate* which subsequently lead to ***I****mpacts* (on human ***W****elfare*). This will then require ***R****esponses* (of ***M****easures*) to reduce different environmental pressures. In EMERGE, the DAPSIR concept will be used to structurally assess how the activity of shipping poses pressures on the marine environment and how those pressures may change the state of the environment and cause impacts on the marine environment and on human welfare.

The framework is described in Figure 1 and starts with the driver which is referred to as human needs and comprises e.g. food, shelter, goods, services and leisure. In order to obtain this, society carries out activities including shipping, agriculture, leisure activities; all causing pressure on the environment. In EMERGE, only the link between drivers and the activity "shipping" is considered. The shipping sector is in EMERGE separated into different ship types, e.g. tankers, passenger ships and container ships, since the volume (and pressure) of different waste streams differs between ship types. For example, the volume of grey water is correlated to the number of persons onboard, implying that cruise ships with many passengers produce much larger volumes than a tanker with a handful of people onboard. On the other hand, scrubber discharge water production is dependent on the engine load and the installed power of the engines connected to the scrubber. The waste streams contain different environmental stressors (here referred to as pressure categories). For example, scrubber discharge water contains acidifying compounds, contaminants and nutrients. These pressure categories can further be subdivided to pressure subcategories, e.g. contaminants can be subdivided to metals, organic compounds and oil residues. The term oil residues refer to pollutants associated with oil use and include both inorganic and organic compounds in solid or liquid phase. As the knowledge regarding discharge and impact of particles and oils derived from scrubber use is limited this is not further investigated within the scope of this report. Each pressure subcategory ultimately poses a pressure on the marine environment, which may change the *state* of the environment. In this framework, the state indicators included are marine acidification, marine ecotoxicity and marine eutrophication.

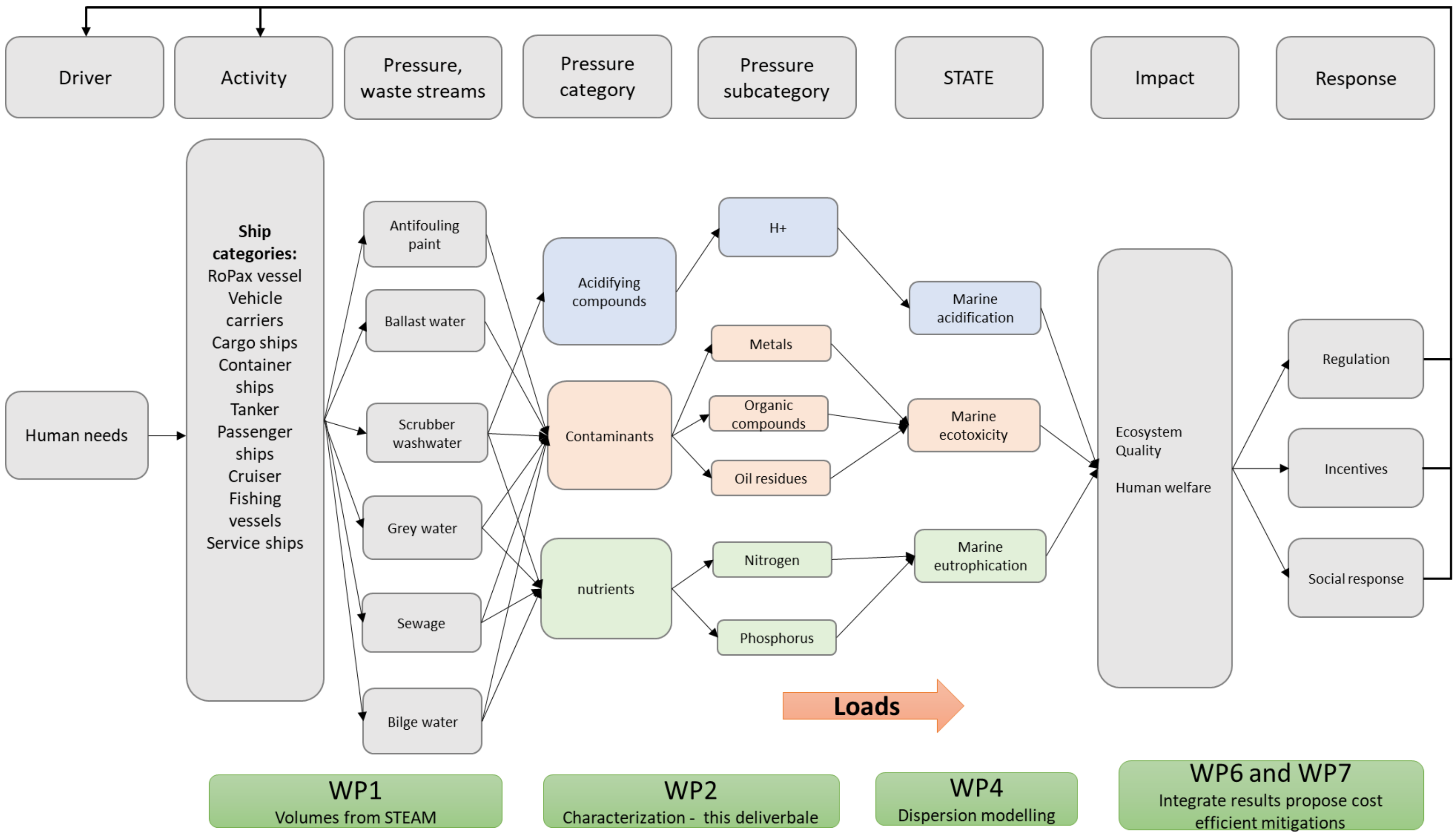

Figure 1. The DAPSIR framework used in EMERGE to investigate how pressures from shipping may change the environmental state and cause impacts on marine ecosystems and human welfare.

3 Material and methods

An extensive literature review to characterize waste streams from shipping with respect to contaminants and nutrients has previously been conducted in the EU BONUS project SHEBA (Sustainable Shipping and Environment of the Baltic Sea region https://www.sheba-project.eu/). The data presented in this deliverable is built on the SHEBA project, but with updated emission factors from recent studies. The main focus is on scrubber discharge water, but emission factors of contaminants and nutrients from other waste streams have also been compiled.

3.1 Scrubber water

The data was compiled from reports and open access publications available as of May 2020 (Supplementary info - D.2.1.WasteStreams.xlsx). The different sampling campaigns used a variety of approaches when performing and reporting the specific methods, presenting the results (including data) and providing background information. Comparison of main findings of each data source are presented in table Table 1. The data originate from sampling campaigns conducted between 1993-2018, published from 2005 to 2020. The entire dataset includes measurements from a variety of vessels, equipped with closed and/or open loop scrubber systems on their main and/or auxiliary engine, as well as samples from the ambient water. In this report, the ambient water samples are defined as the samples collected in ports and marinas as part of a measuring campaign and should not be confused with pristine water.

All references used for data compilation are listed in table Table 1 and a brief description of their respective contribution is found in table Table 2. Two thirds of the publications are non-peer-reviewed reports. Most datasets include information of the year when sampling was conducted, but lack further details regarding the season of sampling, at what geographical position sampling was done and the mode of operation of the engine, e.g. the engine load and % of maximum continuous rating (MCR) of the engine(s) connected to scrubbers, fuel content and wash water flow rate. The mode of operation of the engine, sulphur content of the fuel and the discharge rate of the scrubber water have been included in the database where applicable (Supplementary info). The spatial distribution indicates that Northern Europe (the North Sea and the Baltic Sea with adjacent ports) is overrepresented in the previous sampling campaigns.

The mode of operation of the scrubber, i.e. closed or open loop, is always reported, but details regarding treatment steps of the specific setups were usually lacking. Especially for open loop scrubbers, where treatment is not mandatory and rarely used, this will be of importance when measuring discharge water concentrations. If not stated otherwise, it is assumed that the sampling of scrubber discharge water is performed before any additional dilution of the discharge water, e.g. mixing with cooling water.

During some of the sampling campaigns, additional samples have been taken at different locations of the scrubber system, usually when it is operated in closed loop. The different steps are not discussed further but the data is available in the Supplementary info (D.2.1.WasteStreams.xlsx), classified as “other”. The concentration of the sludge is often reported as mass-per-mass instead of mass-per-volume.

During the Hufnagl et al. (2005) campaign, extensive sampling was performed in the ports of Calais and Dover over the course of one year, and the Koski et al. (2017) campaign took samples in the port of Copenhagen; these are included in this document to represent ambient water.

Table 1: Data sources listed with their respective reference number. The reference numbers coincide with the numbers designated to each dataset in the Supplementary info. Some references have been partly or fully excluded from the data analysis and are denoted with a star.

Ref. nr	Reference
1	IMO MEPC 73/INF.5. Marine Environmental Protection Committee, International Maritime Agency (IMO). 20 July 2018. Study report on analysis of water samples from exhaust gas cleaning systems.
2	MARINTEK (Buhaug et al. 2006). MARULS WP3: Washwater Criteria for Sea Water Exhaust Gas SOx Scrubbers. Prepared by the Norwegian Marine Technology Research Institute (MARINTEK) for the Norwegian Shipowners' Association/Research Council of Norway. November 2006.
3	US EPA. 2011. Exhaust Gas Scrubber Washwater Effluent. United States Environmental Protection Agency. Office of Wastewater Management Washington, DC 20460. EPA-800-R-11-006. November 2011.
4	Kjølholt, J. S., S. Aakre, C. Jürgensen, and J. Lauridsen. 2012. Assessment of possible impacts of scrubber water discharges on the marine environment. Environmental Project No. 1431. Danish Ministry of the Environment. Environmental Protection Agency.
5	IMO PPR 6/INF .20. 2018- Review of the 2015 guidelines for exhaust gas cleaning systems (Resolution MEPC.259(68)). Results from a German project on washwater from exhaust gas cleaning systems. Submitted by Germany.
6	Hufnagl, M., G. Liebezeit, and B. Behrends. 2005. Effects of SeaWater Scrubbing. BP marine.
7	Turner, D. R., I.-M. Hassellöv, E. Ytreberg, and A. Rutgersson. 2017. Shipping and the environment: Smokestack emissions and scrubbers. Elementa 5.
8	Magnusson, K.; Thor, P.; and Granberg, M., 2018. Risk Assessment of marine exhaust gas EGCS water, Task 2, Activity 3, EGCSs closing the loop, IVL Swedish Environmental Research Institute, Report B 2319
9*	Hansen 2012. Exhaust Gas Scrubber Installed Onboard MV Ficaria Seaways Public Test Report Environmental Project No. 1429, 2012
12	IMO MEPC 74/INF.24 Report on the environmental impact assessment of discharge water from exhaust gas cleaning systems. Submitted by Japan 2019.
13	Koski M., Stedmon C., Trapp S. 2017. Ecological effects of scrubber water discharge on coastal plankton: Potential synergistic effects of contaminants reduce survival and feeding of the copepod *Acartia tonsa*, Marine Environmental Research
14	Ushakov, S., Stenersen, D., Einang, P.M. et al. 2019. Meeting future emission regulation at sea by combining low-pressure EGR and seawater scrubbing. J Mar Sci Technol.
15	Johannes Teuchies , Tom J.S. Cox, Katrien Van Itterbeeck et al. 2020. The impact of scrubber washwater on inland waters, 23 April 2020, PREPRINT (Version 1) available at Research Square. DOI: 10.21203/rs.3.rs-23441/v1
16*	DNV-GL & Carnival Corporation & PLC Report 2019. Compilation and Assessment of Lab Samples from EGCS Washwater Discharge on Carnival Ships. http://media.corporate-ir.net/media_files/IROL/14/140690/Carnival-DNVGL_Washwater_Analysis_2018.pdf
17*	Ytreberg E., Hassellöv I-M., Nylund A.T., Hedblom M., Al-Handal A. Y., Wulff A. 2019. Effects of scrubber washwater discharge on microplankton in the Baltic Sea. Marine Pollution Bulletin. https://doi.org/10.1016/j.marpolbul.2019.05.023.

The term “ambient water” refer to the water samples taken as part of a scrubber sampling campaign, without being sampled directly from a ship equipped with a scrubber. This can be compared to “inlet water” samples that are taken from the ship. Ambient water should not be confused with pristine conditions but is rather representing harbour conditions from three European ports (Dover, Calais and Copenhagen).

Different campaigns focused on different parameters (Table 2), but all campaigns measured and reported metals and major ions of the discharge water. Many campaigns also included organic compounds, where non substituted polycyclic aromatic compounds (PAHs) were overrepresented. Other organic compounds reported were alkylated PAHs, size fractions of hydrocarbons, dioxins and BTEX (benzene, toluene, ethylbenzene and xylenes).

It is not always clarified what analytical methods that have been used and if the reported concentrations correspond to the total concentration, the dissolved fraction or the particulate fraction. Implications of this will be further discussed as a potential source of uncertainty and variability of the compiled dataset.

Average concentration, with the 95% confidence interval, was calculated for each compound found in the different solutions; the open loop inlet water, the open loop discharge water, the closed loop discharge water and the ambient water. All values being reported as below LOD/LOQ, where the limits have been specified, have been included in the dataset as ½ LOD (or ½ LOQ). Three datasets were not included in the calculations of average and confidence interval (denoted with a star in Table 1). These where 1) the data from Ytreberg et al. (2019) where a scrubber in an engine lab was used, 2) the results of closed loop scrubber discharge of Hansen (2012) due to the extremely high detection limit (more than 2 orders of magnitude higher than other), skewing the average and 3) the dataset from DNV-GL and Carnival Corporation & PLC (2019); where no raw data was obtained and the reported values were averages of the entire dataset without any measure of variability and dispersion. In the report, where the data was summarised, the units were not reported in the table and had to be assumed. Both DNV-GL and Carnival Corporation & PLC were contacted with requests of sharing the raw data, but no answer has been provided.

The average concentrations were also used when calculating emission factors (mg/MWh) based on different scrubber scenarios. The emission factors (mg/MWh) were calculated from the average concentrations of each analyte in the discharge water (mg/m^3) times the determined discharge flow rates (m^3/MWh) for open and closed loop, resulting in a unit of mass pollutant released for every MWh used (Equation *2*). The emission factors were calculated according to Equation *2*:

Equation 2 $$EF_i = c_i \times discharge\ flow\ rate$$

Where c_i is the average concentration (µg/L) of contaminant *i* and the discharge flow rate (m^3/MWh) was calculated by dividing the water flow rate (m^3/h) with the power of the combustion engine being scrubbed (MW), Equation *3*.

Equation 3 $$discharge\ flow\ rate = \frac{scrubber\ inlet\ water\ flow}{engine\ load\ at\ time\ of\ scrubbing}$$

Since not all sources reported the discharge flow rate or the other parameters used to calculate the discharge flow rate, a sensitivity analysis was performed to ensure that the calculated emission factors were representative for the dataset.

*Table 2: An overview of the information provided from each reference and sampling campaign. × marks where information has been provided, not specifying the level of detail, and the - marks where information is missing or lacking. OL/CL is open and closed loop respectively. Additional information of sampling, is exemplified in the "other" column: "Steps CL" means data is provided from several stations of the closed loop system, "Ambient" means that samples from ambient water has been analysed, "Sludge" marks where the sludge of CL has been analysed and "Dilution" where sampling has been done before and after dilution with reaction water. For chemical parameters; Tot. means that the total concentration is given but no information about speciation or specific compounds are available and "other" shows where additional information is provided. Etc includes alkalinity, dioxins and HCB. For the analysis part; it is investigated if there is any information regarding phase (dissolved or particulate Diss./Part.) of the analytes and the analytical methods used to quantify metals, PAHS and other constituents. *including two unpublished metal analysis results from the same sampling campaign. **unfiltered metal samples personal communication*

Study			Environment			Scrubber setup		Sampling			Chemical parameters					Analysis			
Ref.	Year	Peer-review	Time	Position	Mode of operation	OL/CL	Cleaning step (OL)	Inlet	Outlet	Other	Metals	PAH	BTEX	N	Other	Diss./ Part.	Anal. Method [Me, PAH, other]		
1	2018	-	×	×	×	×	-	×	×	-	×	×	Tot.	×		×	×	×	×
2	2006	-	×	-	×	×	-	-	×	-	×	Tot.			pH, SPM, THC	-	×	×	×
3	2011	-	-	-	-	×	×	-	×	-	×	-	-	Tot.		×	-	-	-
4	2012	-	×	×	×	×	-	×	×	Steps CL	×	Tot.	-	Tot.	pH, SPM, THC	×	-	-	-
5	2018	-	×	×	×	×	-	×	×	-	×	×	-	×	SPM, Alk, Me-Naph	×	×	×	×
6	2006	-	×	×	-	×	-	×	×	Ambient Steps CL	×	×	-	×		×	×	×	-
7*	2017	×	×	-	-	×	-	-	×	-	×	-	-	-	-	×	×	-	-
8	2018	-	×	-	-	×	-	×	×	Steps CL Sludge	×	×	×	×	Alkylated PAH, pH, THCs etc.	-**	-	-	-
9	2012	-	×	-	×	×	-	×	×	Sludge	×	-	-	-	-	-	-	-	-
12	2019	-	×	-	×	×	-	×	×	-	×	×	-	-	Organics, pH	-	-	-	-
13	2017	×	×	×	-	×	-	×	×	Ambient	×	-	-	-	pH	-	×	-	-
14	2020	×	×	×	×	×	×	×	×	Dilution	×	×	-	×	pH, THCs	-	×	×	×
15	2020	Pre-print	×	×	×	×	×	×	×	Steps CL	×	×	×	-	PCB, THCs, pH	-	×	×	-
16	2019	-	×	-	-	-	-	×	×	-	×	×	-	-	-	×	-	-	-
17	2019	×	×	×	×	×	-	×	×	-	×	-	-	-	-	×	×	-	-

3.2 Grey water

Grey water is the common name for drainage from dishwater, shower, laundry, bath and wash basin drains. Emission factors were obtained from Ytreberg et al. (2020) where contaminants and nutrients in grey water have been compiled in an extensive literature review.

3.2.1 Concentrations of contaminants in grey water

The compilation by Ytreberg et al. (2020) is based on data mainly from cruise ships operating in Alaska during 2000 to 2013 (ADEC Alaska Department of Environmental Conservation 2000, 2002, 2004, 2005, 2006, 2007, 2008, 2009, 2010a, b, 2011, 2012, 2013) apart from on study by Madjidian and Rantanen (2011) which was performed on ships in the Baltic Sea. The data comprises 86 onboard samples analysed for 44 different contaminants (28 organic compounds and 16 metals/elements). When a specific contaminant was reported as “not detected” in the reports, ½ the limit of detection (LOD) or ½ the limit of quantification (LOQ) was used as default value (US EPA 2000). In the case where neither LOD nor LOQ were reported, a value of zero was used for not detected contaminants.

3.2.2 Concentrations of nutrients in grey water

Concentrations of nutrients (nitrogen species and total nitrogen and total phosphorous concentrations) are based on 17 reports containing in total 159 samples from 30 cruise ships sampled in Alaska from 2000 to 2013 (ADEC Alaska Department of Environmental Conservation 2002, 2004, 2005, 2006, 2007, 2008, 2009, 2010b, 2011, 2012, 2013) (USEPA 2006a, b, c, d). As for the contaminants, ½ LOD or ½ LOQ was used for not detected values and when neither LOD nor LOQ was reported a value of zero was used.

3.3 Sewage

Sewage, or sometimes called black water, contains contaminants and nutrients. Less investigated, and not included in this report, is the potential content of pathogens.

3.3.1 Concentrations of contaminants in sewage

Concentrations of contaminants in sewage were also obtained from the same ADEC studies as grey water (ADEC Alaska Department of Environmental Conservation 2000, 2004, 2005, 2006, 2007, 2008, 2009, 2010b, 2011, 2012, 2013) (Madjidian and Rantanen 2011) but also includes a study by US EPA (2008). Metals have been analysed in 95 samples and comprises both dissolved and total concentrations of 16 different metals/elements. For organic compounds, in total 51 compounds have been analysed in 108 different samples. Non detected values were treated as described under the grey water section.

3.3.2 Concentrations of nutrients in sewage

The data collection of nutrients (in the forms of nitrogen and phosphorous) in sewage were derived from Ytreberg et al. (2020) and can be found in Supplementary Info (D.2.1.WasteStreams.xlsx).

3.4 Bilge water

Bilge water contains a mixture of condensed water from the engine room, fuel oil, cleaning agents and residuals from lubricants (Magnusson et al. 2018a). In total, 52 different contaminants including petroleum compounds, PAHs, metals, detergents and other organic compounds have been identified. The data set includes measurements on 49 treated bilge water samples. Non detected values were treated as described under the grey water section.

3.5 Ballast water

Currently, 40 different Ballast Water Management Systems (BWMS) are approved by IMO to be used on ships. During the approval process the applicant must show that the active substances used in the BWMS do not pose unreasonable risk to the environment, human health, property or resources. Therefore, concentrations of active substances, degradation compounds and biproducts from the different BWMS have been compiled from reports submitted to IMO's Marine Environment Protection Committee (MEPC). In total 129 different compounds have been identified in effluent water from the different BWMS.

3.6 Antifouling paints

Release rates (in µg/cm^2/day) of copper, zinc, zinc pyrithione, copper pyrithione, DCOIT and Zineb were compiled from regulatory agencies and scientific literature (California Department of Pesticide Regulation 2015; New Zealand EPA 2013; Ytreberg et al. 2010). As antifouling coating application is known to vary in different marine environmental regimes, four different categories of antifouling coatings were defined:

A. As the Gulf of Bothnia and, to a less extent, the Baltic Proper are subjected to ice conditions, many ships use a non-toxic epoxy-coating instead. For the ships operating only in Gulf of Bothnia, it was assumed that 20% used antifouling paint, similar to the assumption made the Finnish Environmental Institute recommend (SYKE 2003).
B. For ships operating in the Baltic Proper only, a 50% antifouling coating application rate was assumed, i.e. as recommended by the Swedish Chemical Agency (Ambrosson 2008)
C. For ships operating between the Baltic Sea and Kattegat, 100% of the ships were assumed to be coated with antifouling paints
D. internationally (areas outside of the Baltic Sea and Kattegat) 100% of the ships were assumed to be coated with antifouling paints.

Different release rates of copper, zinc, zinc pyrithione, copper pyrithione, DCOIT and Zineb were applied to the different AF categories depending on the regulatory framework where higher release rates were expected for category D, followed by category C and lower release rates for category B and A. As the antifouling paint market is dominated by copper- and zinc-based coatings, we assumed that if an antifouling coating were used, 100% of them contained and released copper and zinc to the environment and only 20% of the coatings contained and released the booster biocides zinc pyrithione, copper pyrithione, DCOIT and Zineb.

3.7 Characterization of a model ship used to compare loads of contaminants from different waste streams

A RoPax model ship, with design and operational properties typical for RoPax ships operating in the Baltic Sea (Table 3), was used to compare yearly loads of contaminants from different waste streams. Firstly, the yearly discharge volumes from the different waste streams were calculated based on an operating time of 4546 hours per year. Secondly, the volumes were multiplied with the average concentration of the specific contaminants present per waste stream. This was conducted for all waste streams except antifouling where the underwater surface area was multiplied with the release rate of biocides to obtain the yearly load. The number of passengers and crew was assumed to be 1450. The production rate of grey water (157 L/person-day) and sewage (33.1 L/passenger-day) are from DNV (2009) where all of the waste water streams were expected to be discharged back to the sea. The ship was assumed to have an open loop scrubber for SO_2 abatement with a discharge rate of 90 m^3/MWh.

Table 3. Data for the Baltic Sea model ship used in the analysis.

Parameter	Value	Unit
Ship Type	RoPax (ferry)	-
Gross Tonnage	40000	-
Main engine size	23	MW
Auxiliary Engine size	6.5	MW
Passengers and crew	1450	Persons
Operating time	4546	Hours/year
Under water surface area	5000	m^2
Scrubber	Open loop	
Antifouling paint	Category C	
Grey water	157	L/person-day
Black water	33.1	L/person-day
Bilge water	3400	L/day
Scrubber water	90	m^3/MWh

4 Results and discussion

In this report, only the key findings in terms of characterization of the different waste streams are presented. Individual measurements of contaminants, nutrient and acidifying compounds (pH) from the different pressures (scrubber water, antifouling paints, ballast water, grey water, sewage and bilge water) are however available in the Supplementary info (D.2.1.WasteStreams.xlsx) and can be used for additional assessments.

4.1 Scrubber water

All parameters reported have been included in the Supplementary info (D.2.1.WasteStreams.xlsx) and is available for further analysis. This section will focus on some of the major findings of the data compilation. It is apparent that the reported concentrations of contaminants and nutrients vary significantly between the different sampling campaigns and, also, within the same sampling campaign. There can be several reasons for this, such as fuel type, engine type, scrubber manufacturer, whether the open loop system is fitted with a cleaning step, where the samples are collected and how the samples are collected. This will not be discussed in detail, but it is important to be aware of the large variability and the potential explanations.

The different parameters are presented according to the pressure categories in Figure 1, where the pressures can be acidifying compounds, contaminants or nutrients. Some compounds contribute to several pressures and are thus part of more than one category.

4.1.1 Acidifying Compounds

As explained in the introduction, the main purpose of the scrubber is to remove SO_X from the exhaust gas. It has proven to be an efficient method if alkalinity is kept high enough, either by using a high seawater flow or by adding an alkaline salt such as sodium hydroxide (NaOH). The dissolution of SO_X species in water will result in three things: an increase of sulphur in the water, a decrease of pH, due to the formation and dissociation of sulphuric acid, and a consumption of alkalinity, when buffering the change in acidity. Very few campaigns measure the alkalinity of the inlet and the discharge water, but pH and sulphur content of the scrubber discharge water are reported to some degree (compilation in Table 2).

As expected, the lowest average pH (based on measurements listed in table 2) is that of the open loop scrubber water discharges. The closed loop discharge waters have been treated with a base, e.g. NaOH, which results in higher pH of the water being discharged. Comparing the pH values of open loop waters in Table 4, it is evident that the pH of the discharge waters is significantly lower than the pH of the inlet water, but it also found that the inlet water, already prior to scrubbing, has a lower pH than ambient water. This shows that inlet water should not be considered a comparable reference, equivalent to ambient or pristine conditions. Ushakov et al. (2020) compared the pH in scrubber discharge when measuring according to IMO standards, without any dilution, and according to US-EPA standards, when the discharge water is further diluted with more seawater, called reaction water. Without dilution the pH was 3.24 and with dilution the pH was 6.52. Since it is not always specified where in the scrubber outlet the pH is measured, the values of Table 4 should be treated with caution.

While sulphur, as sulphate, is a major constituent of natural seawater without known harmful effects, it can be valuable to compare the inlet vs. the discharge water to assess the efficiency of the scrubber process. Sulphate might also precipitate and form gypsum ($CaSO_4$), sodium sulphate (Na_2SO_4) or other solids that could flocculate and affect the measured concentrations of sulphur but also other constituents of seawater. Sulphur content is measured with different approaches where some campaigns measure the total sulphur content and others measure the sulphate ion concentration, explaining some of the variability demonstrated in Table 4.

Pristine conditions are not listed in Table 4 due to large variations seen in both pH and sulphate concentration. In general, the sulphate concentration is considered conservative and will thus follow the salinity of the seawater. pH is more complicated as it is dependent on temperature, salinity and pressure as well as biological activity, e.g. photosynthesis and respiration.

Table 4: Average values of pH and sulphur concentrations, including 95% confidence interval, for open and closed loop discharge water, open-loop inlet water and ambient water. The ambient category represents primarily harbors and marinas where sampling of the surrounding water has been made. N= number of studies included. The average and confidence interval of pH is calculated from the 10^{-pH} values, i.e. the $[H^+]$.

	Open loop scrubber discharge		Open loop inlet water		Closed loop scrubber discharge		Ambient water	
	$\bar{X}$ ± 95% CI	N	$\bar{X}$ ± 95% CI	N	$\bar{X}$ ± 95% CI	N	$\bar{X}$ ± 95% CI	N
pH	3.85 ± 0.33	36	7.72 ± 0.14	29	4.54 ± 0.51	11	8.08 ± 0.07	38
Sulphur (mg/L)	2200 ± 446	18	2376 ± 480	13	12280 ± 10104	9	2645 ± 382	13

4.1.2 Contaminants

In Figure 1, the pressure categories are divided into three subcategories of metals, organic compounds and oil residues. For this section, metals and PAHs are primarily considered since this is where most data exist. All subcategories are represented in scrubber discharge water but can also originate from other sources, mainly anthropogenic ones connected to human activities.

The parameters, if not stated otherwise, are expressed in total concentration. It should be noted that information of the reported concentrations, and if the values represent the total or dissolved fraction, is sometimes lacking. For the parameters that have been reported as both dissolved and particulate, the sum is presented in the excel sheet. If both fractions were below the limit of detection (LOD) or limit of quantification (LOQ), this is marked with orange colour, and if one of the fractions were below LOD/LOQ, this is marked with yellow.

4.1.2.1 Metals and inorganic elements

Several elements are represented in the Supplementary info, both major ions, such as sodium and magnesium, present in high concentrations in natural seawater, and trace elements, such as copper and vanadium, less common to find in high levels of unpolluted seawater. In Table 5, the average concentration and the 95% confidence interval of all inorganic trace elements that were measured and detected during the previous sampling campaigns, listed in table 1 and 2, are included. The concentrations of the same elements found in the inlet water, in the ambient environment and in pristine surface seawater are also included. The values of the ambient category are based on measurements in harbours and marinas, primarily port of Calais and port of Dover in 2004 (Hufnagl et al. 2005). Since ports often are subject to several stressors and input of pollutants the pristine category was added to Table 5 to represent reference values. The values are based on data published in Bruland and Lohan (2003).

Regarding open loop systems, the inlet water has similar concentrations as the outlet water for many of the compounds. This could be an indication of an already polluted environment, making the additional contribution from scrubbers seemingly small. There can be several reasons for the high concentration of metals found in the open loop inlet water. Depending on where on the ship the sampling is conducted, the water can be affected by the antifouling paint containing copper and zinc, the “sacrificial anodes” often made of zinc, and copper and aluminium anodes to prevent biofouling on the hull and in the cooling water piping. In addition, neighbouring vessels can discharge polluted water that is later being used as inlet water on another ship. The low pH of scrubber water changes the chemical speciation of the metals and might promote a higher degree of release of metals from the ship and other metal containing structures. The concentrations of nickel and vanadium are significantly higher in the discharge water than in the inlet water. Selenium has only been measured in the open loop discharge water and shows a significant increase compared to the pristine water concentrations.

Table 5: Average total * *concentration of trace elements found in scrubber discharge water, presented with a 95 % confidence interval. The ambient category represents primarily harbors and marinas where sampling of the surrounding water has been made. The pristine category represents an unpolluted surface water where the concentrations have been derived from Bruland and Lohan (2003). N= number of studies included.*

**total concentration is the sum of particulate and dissolved, if not specified it is assumed to be the total concentration.*

	Open loop scrubber discharge		Open loop inlet water		Closed loop scrubber discharge		Ambient water		Pristine water
	$\bar{X}$ ± 95% CI (µg/L)	N	$\bar{X}$ ± 95% CI (µg/L)	N	$\bar{X}$ ± 95% CI (µg/L)	N	$\bar{X}$ ± 95% CI (µg/L)	N	(µg/L)
Arsenic	6.99 ± 3.58	62	5.81 ± 1.46	52	23.00 ± 10.21	22	1.45 ± 0.64	2	1.9
Barium	14.69 ± 4.81	5	14.44 ± 4.98	6	-	-	19 ± 12.7	13	15
Cadmium	0.85 ± 0.3	62	0.99 ± 0.33	54	0.58 ± 0.20	22	0.145 (<LOD)	2	0.07
Chromium	14.53 ± 6.35	59	16.3 ± 18.41	52	1250 ± 2045	16	0.43 ± 0.5	2	0.21
Cobalt	0.17 ± 0.14	6	0.07 ± 0.06	4	-	-	-	-	0.0018
Copper	38.75 ± 12.45	70	28 ± 14	58	519.42 ± 243.64	23	73.78 ± 314	3	0.19
Lithium	180 ± 5.06	10	177 ± 4.9	10	-	-	169.92 ± 20	13	179
Lead	9.20 ± 4.48	67	8.27 ± 4.95	55	8.24 ± 3.36	22	0.045 (<LOD)	2	0.002
Mercury	0.08 ± 0.01	26	0.08 ± 0.02	22	0.07 ± 0.02	16	-	-	0.0002
Molybdenum	10.69 ± 0.95	7	10.72 ± 0.85	5	66	1	-	-	10
Nickel	46.86 ± 11.25	65	8.83 ± 4.5	54	2623 ± 854	22	0.4 (<LOD)	2	0.47
Selenium	97.00 ± 38.12	2	-	-	-	-	-	-	0.13
Vanadium	176.59 ± 49.96	61	9.45 ± 5.29	50	1402 ± 3450	22	0.625 ± 0.064	2	1.7
Zinc	110.84 ± 60.87	70	175.58 ± 147.25	56	387.71 ± 222.64	22	6.2 ± 35.58	2	0.33

For closed loop systems, the data is scarcer and the uncertainties greater. Most elements are present in higher concentrations in the closed loop discharge water than in the open loop discharge water. This would be an indication of accumulation of metals from the combustion and scrubber process since freshwater is often used in the closed loop scrubber system. Cadmium and mercury do not follow the same trend as some of the other metals and seem to be smaller in the closed loop discharge water when considering the entire dataset. This could be due to a larger accumulation in the particulate fraction, settling as sludge (Magnusson et al. 2018a) did however report of elevated mercury concentrations in the closed loop bleed-off discharge water, contradicting the trends seen in Table 5.

For the inorganic elements, where the LOD values sometimes vary with several orders of magnitude, the ½ LOD values can have huge implications on the calculated average concentrations, including the confidence interval, in the scrubber discharge water. Table 6 shows the total number of measurements included in the calculation of average and confidence interval and how many percent of the measurements that were below LOD. Nickel and vanadium have a high detection rate in both open and closed loop discharge while cadmium and mercury are rarely found in concentrations above LOD.

Table 6: Proportion of LOD/LOQ values for trace elements, expressed as the fraction (in %) of the total number of measurements (N) included in the average concentration calculations presented in Table 5.

	Open loop scrubber discharge		Open loop inlet water		Closed loop scrubber discharge		Ambient water	
	% below LOD	N	% below LOD	N	% below LOD	N	% below LOD	N
Arsenic	69.4	62	75	52	22.7	22	0	2
Barium	0	5	0	6	-	-	0	13
Cadmium	88.7	62	94.4	54	81.8	22	100	2
Chromium	47.5	59	71.2	52	53.3	15	0	2
Cobalt	66.7	6	75.0	4	-	-	-	-
Copper	25.7	70	41.2	58	4.5	22	0	3
Lithium	0	10	0	10	-	-	0	13
Lead	55.2	67	74.5	55	63.6	22	100	2
Mercury	76.9	26	86.4	22	68.7	16	-	-
Molybdenum	0	7	0	5	0	1	-	-
Nickel	4.6	65	59.3	54	0	22	100	2
Selenium	0	2	-	-	-	-	-	-
Vanadium	0	61	64.0	50	0	22	0	2
Zinc	28.6	70	51.8	56	9.1	22	0	2

4.1.2.2 **Organic compounds**

There are several organic compounds present in the scrubber discharge water, mainly originating from the fuel and the combustion of the fuel. Polycyclic aromatic hydrocarbons (PAHs) are, next to metals, the most studied constituents of scrubber discharge water (Table 7).

All average concentrations of PAHs, including the 95% confidence interval, for discharge water, scrubber inlet water, ambient water and pristine surface seawater is presented in Table 8. The values of the ambient category are again based on measurements in harbours and marinas, primarily port of Calais and port of Dover in 2004 (Hufnagl et al. 2005). The PAHs are listed based on the molecular weight, with the low molecular weight compounds at the beginning and higher molecular weights the further down in the table.

The concentrations of some of the measured PAHs are higher in the scrubber discharge water of both open and closed loop systems compared to the inlet water indicating that; 1) the sources of PAHs can be derived to the scrubber process and 2) that the cleaning steps of the closed loop systems are insufficient. Again, the ambient and inlet water concentrations are much higher than the pristine concentrations, showing that these areas are already polluted to some degree. The variability in the dataset is also true for the PAHs, but the differences between ambient/inlet water and the discharge water associated to the scrubbing process illustrates a clearer connection between scrubbers and increased pollution.

Table 7: Average total * *concentration of organic compounds found in scrubber discharge water, presented with a 95 % confidence interval. The ambient category represents primarily harbors and marinas where sampling of the surrounding water has been made. The pristine category represents an unpolluted surface water where the concentrations have been derived from Law et al (1997). N= number of studies included.*

**total concentration is the sum of particulate and dissolved, if not specified it is assumed to be the total concentration.*

	Open loop scrubber discharge		Open loop inlet water		Closed loop scrubber discharge		Ambient water		Pristine water
	$\bar{X}$ ± 95% CI (µg/L)	N	$\bar{X}$ ± 95% CI (µg/L)	N	$\bar{X}$ ± 95% CI (µg/L)	N	$\bar{X}$ ± 95% CI (µg/L)	N	(µg/L)
Naphthalene	2.76 ± 0.79	55	0.11 ± 0.08	48	2.08 ± 1.13	18	0.003	1	< 0.010
Acenaphthylene	0.13 ± 0.07	63	0.11 ± 0.11	60	0.08 ± 0.07	11	0.006 ± 0.002	32	< 0.003
Acenaphthene	0.19 ± 0.07	63	0.01 ±0.003	60	0.49 ± 0.39	11	0.011 ± 0.005	32	< 0.002
Fluorene	0.46 ± 0.10	63	0.07 ± 0.06	60	1.27 ± 0.67	11	0.018 ± 0.006	32	< 0.001
Phenanthrene	1.51 ± 0.30	64	0.09 ± 0.08	61	4.30 ± 1.98	12	0.072 ± 0.023	32	< 0.008
Anthracene	0.08 ± 0.05	63	0.02 ± 0.02	60	0.14 ± 0.11	11	0.010 ± 0.003	32	< 0.001
Fluoranthene	0.16 ± 0.05	63	0.03 ± 0.02	59	0.35 ± 0.28	11	0.030 ± 0.009	32	< 0.001
Pyrene	0.32 ± 0.12	63	0.05 ± 0.04	60	0.37 ± 0.27	11	0.036 ± 0.011	32	< 0.001
Benz(a)anthrancene	0.13 ± 0.06	64	0.03 ± 0.02	61	0.16 ± 0.20	12	0.019 ± 0.009	32	< 0.002
Chrysene	0.19 ± 0.07	63	0.05 ± 0.03	60	0.11 ± 0.08	11	0.025 ± 0.010	32	< 0.002
Benzo(b)fluoranthene	0.04 ± 0.02	63	0.01 ± 0.004	60	0.04 ± 0.03	11	0.010 ± 0.004	32	< 0.001
Benzo(k)fluoranthene	0.01 ± 0.01	49	0.01 ± 0.004	47	0.02 ± 0.02	11	0.003	1	< 0.001
Benzo(a)pyrene	0.05 ± 0.02	64	0.01 ± 0.004	61	0.04 ± 0.04	12	0.042 ± 0.063	32	< 0.001
Dibenzo(a,h)anthracene	0.03 ± 0.02	63	0.02 ± 0.01	60	0.02 ± 0.02	11	0.006 ± 0.001	32	< 0.001
Benzo(g,h,i)perylene	0.02 ± 0.01	63	0.009 ± 0.004	60	0.02 ± 0.02	11	0.005 ± 0.001	32	< 0.001
Indeno(1,2,3-c,d)pyrene	0.07 ± 0.06	63	0.06 ± 0.06	60	0.02 ± 0.02	11	0.005 ± 0.001	32	< 0.001
Sum EPA 16 PAH	2.97 ± 0.79	35	1.44 ± 2.53	18	17.8 ± 5.3	11	0.303 ± 0.084	31	-
Sum total PAH	7.25 ± 1.95	36	0.4 ± 0.4	28	5.12 ± 3.87	7	-	-	-

Table 8: Proportion of LOD values for organic compounds, expressed as the fraction (in %) of the total number of measurements included in the average concentration calculations presented in Table 7. N= number of studies included.

	Open loop scrubber discharge		Open loop inlet water		Closed loop scrubber discharge		Ambient water	
	% below LOD	N	% below LOD	N	% below LOD	N	% below LOD	N
Naphthalene	1.81	55	72.9	48	0	18	0	1
Acenaphthylene	38.1	63	93.3	60	18.2	11	90.6	32
Acenaphthene	22.2	63	93.3	60	0	11	90.6	32
Fluorene	6.3	63	91.7	60	0	11	78.1	32
Phenanthrene	1.6	64	59.0	61	0	11	12.5	32
Anthracene	27.0	63	100	60	27.3	11	62.5	32
Fluoranthene	11.1	63	74.6	59	0	11	21.9	32
Pyrene	12.7	63	65	60	0	11	6.3	32
Benz(a)anthrancene	37.5	64	73.8	61	33.3	12	21.9	32
Chrysene	27.0	63	73.3	60	27.3	11	25.	32
Benzo(b)fluoranthene	49.2	63	86.7	60	45.5	11	43.8	32
Benzo(k)fluoranthene	83.7	49	93.6	47	81.2	11	0	1
Benzo(a)pyrene	56.3	64	83.6	61	75	12	50.0	32
Dibenzo(a,h)anthracene	84.1	63	98.3	60	81.2	11	90.6	32
Benzo(g,h,i)perylene	65.1	63	93.3	60	72.7	11	71.9	32
Indeno(1,2,3-c,d)pyrene	69.8	63	93.3	60	81.2	11	75.0	32

The higher the molecular weight of the PAH, the more often the concentration is reported as being below LOD. This can have many explanations, one being that the higher molecular weight PAHs will more readily bind to organic matter and particles thus impacting the extraction step before analysis. This demonstrates the importance of measuring, and reporting, both dissolved and particulate fraction of compounds found in scrubber discharge water. The PAHs from the closed loop scrubber discharge have a higher degree of detection (Table 8), reflecting the higher concentrations seen in Table 7.

Some sampling campaigns also reported the total amount of hydrocarbon, alkylated PAHs, size distribution of aliphatic and aromatic hydrocarbons and dioxins. They have not been included in this report due to the small number of measurements but are reported in the Supplementary info (D.2.1.WasteStreams.xlsx).

4.1.3 Nutrients

Nutrients have a natural spatial and seasonal variability that will contribute to the large variability shown in Table 9. It is difficult to draw any conclusions from these data except that it is a challenge to estimate average concentrations, with small confidence intervals, of nitrogen species in the water without considering when, where and how sampling was made. This parameter should rather be considered on a case-by-case basis where the inlet concentrations can be compared to the outlet concentrations to estimate a final load emerging from the scrubber process.

Specifying the forms of the nitrogen species will also indicate whether the water is reduced or oxidised. The larger the fraction of ammonium and nitrite, the more reduced environment, i.e. less oxygen available. This will also affect the speciation of other elements and compounds.

Another potential nutrient is iron. This trace element may be the limiting factor for photosynthetic activity in High Nutrients, Low Chlorophyll (HNLC) areas, and point sources could result in local blooms in areas with otherwise low abundance of phytoplankton. Iron is not only connected to the scrubber system but is widely used in anthropogenic structures such as the ship hulls and piping, which could help explain the huge variety in concentration.

Table 9: Potential nutrients, nitrogen species and iron, concentrations measured in scrubber discharge water from open and closed loop, inlet water associated with open-loop systems and ambient water measured in ports of Dover, Calais and Copenhagen. N= number of studies included.

	Open loop scrubber discharge		Open loop inlet water		Closed loop scrubber discharge		Ambient water	
	$\bar{X}$ ± 95% CI (mg/L)	N	$\bar{X}$ ± 95% CI (mg/L)	N	$\bar{X}$ ± 95% CI (mg/L)	N	$\bar{X}$ ± 95% CI (mg/L)	N
Nitrogen species								
Nitrate (NO_3^{2-})	2.83 ± 2.06	31	3.21 ± 2.23	30	110.98 ± 135.73	4	0.07 ± 0.08	35
Nitrite (NO_2^-)	0.760 ± 0.68	28	0.97 ± 1.28	26	55.76 ± 130.71	4	0.001 ± 0.001	27
Ammonium (NH_4^+)	0.73 ± 0.03	17	0.07 ± 0.04	14	-	-	0.33 ± 0.14	35
Other								
Iron	0.24 ± 0.37	4	0.032 ± 0.08	3	-	-	-	-

4.1.4 Emission factors

For open loop scrubbers, three different scenarios are presented reflecting 1) the discharge rate presented by IMO (45 m^3/MWh), 2) the average discharge rate (90 m^3/MWh) calculated in the Supplementary info (D.2.1.WasteStreams.xlsx) and 3) a worst-case scenario where the higher part of the confidence interval is used for both discharge rate (104 m^3/MWh) and pollutant concentration. For closed loop, the average discharge rate is 0.45 m^3/MWh based on calculations of 8 datapoints, compared to the previously suggested discharge rate of 0.2-0.3 m^3/MWh (IMO 2008). The two closed loop scenarios are calculated based on the two different discharge rates but with the same average concentration. The compound specific emission factors, for each scenario, are found in Table 10.

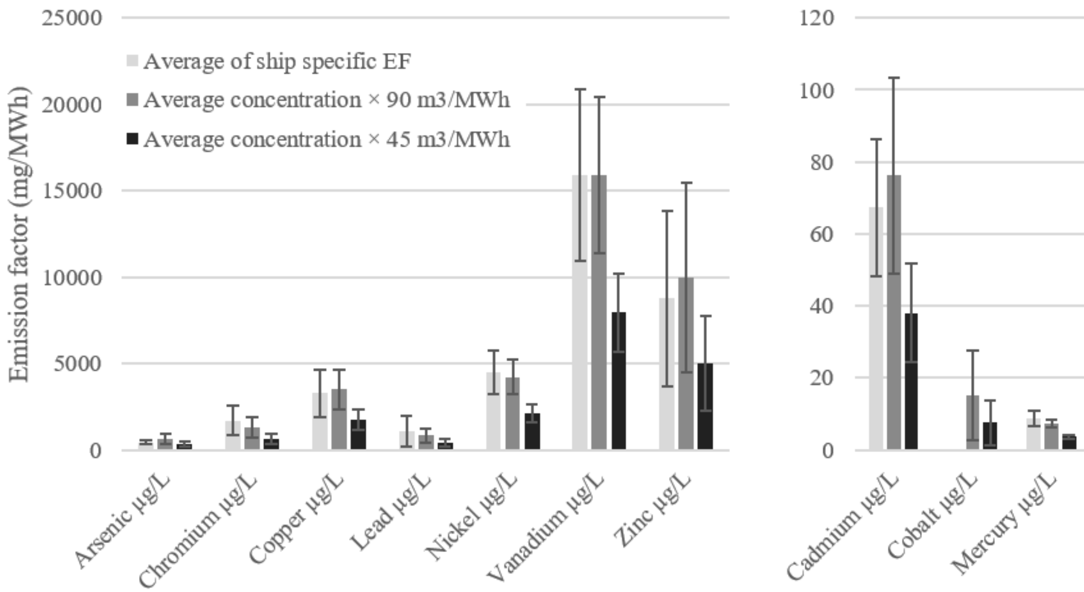

Figure 2: Calculated emission factors from open loop discharge flow rates and trace element content. The light grey bar showing the calculated emission factors when using ship specific discharge flow and concentration of trace elements, the dark grey bar show the calculated emission factors using the average trace element concentrations from discharge water and the average open loop discharge flow of 90 m^3/MWh and the black bar show the calculated emission factors based on the same calculation but using 45 m^3/MWh instead.

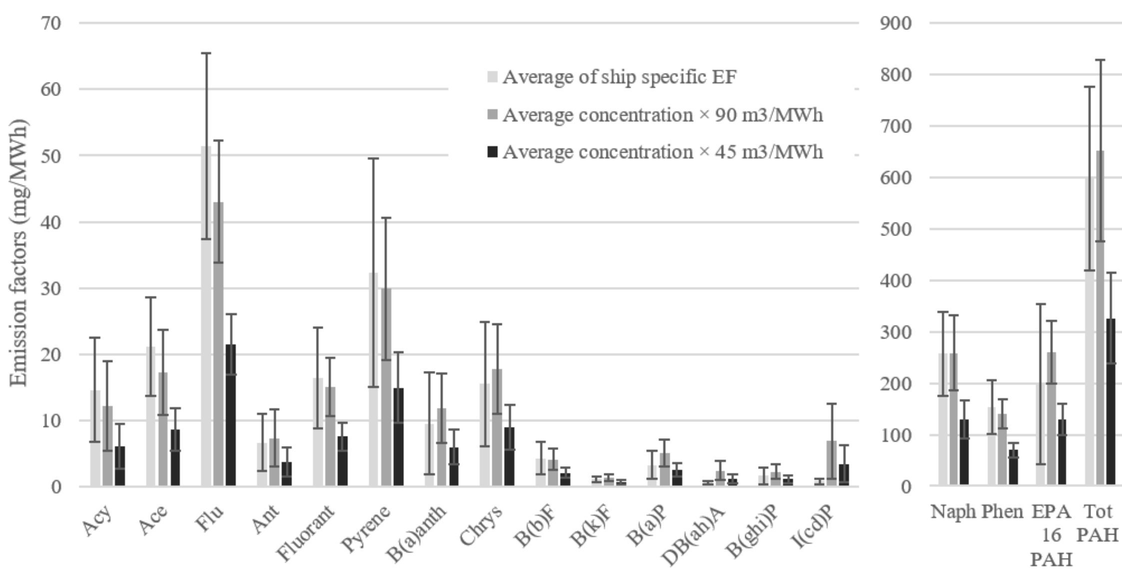

Figure 3: Calculated emission factors from open loop discharge flow rates and PAH content. The light grey bar showing the calculated emission factors when using ship specific discharge flow and concentration of PAHs, the dark grey bar show the calculated emission factors using the average PAH concentrations from all data points and the average open loop discharge flow of 90 m^3/MWh and the black bar show the calculated emission factors based on the same calculation but using 45 m^3/MWh instead.

Table 10: Calculated emission factors based on five different scenarios; two represent closed-loop usage with two different average discharge rates (0.25 m^3/MWh from IMO and 0.45 m^3/MWh from the compiled dataset), two represent open-loop usage with average discharge concentrations and discharge rates of 45 m^3/MWh and 90 m^3/MWh and the final scenario is based on the concentration of the upper value of the confidence interval times the upper value of the confidence interval of the discharge flow.

	Emission factors (mg/MWh)				
	Closed loop scenarios		Open loop scenarios		
	$\bar{X}_i \times 0.25$	$\bar{X}_i \times 0.45$	$\bar{X}_i \times 45$	$\bar{X}_i \times 90$	$(\bar{X}_i + 95\%\ CI) \times 104$
Metals					
Arsenic	5.75	10.35	314	629	1099
Barium	-	-	661	1322	2028
Cadmium	0.14	0.26	38.1	76.2	119
Chromium	312.62	562.73	653	1307	2171
Cobalt	-	-	7.58	15.2	32
Copper	129.86	233.74	1743	3487	5324
Lithium	-	-	8100	16200	19246
Lead	2.06	3.71	414	828	1422
Mercury	0.02	0.03	3.63	7.26	9.77
Molybdenum	16.5	29.7	481	962	1210
Nickel	655.77	1180.39	2108	4216	6042
Selenium	-	-	4365	8730	14052
Vanadium	2350.49	4230.88	7946	15893	23561
Zinc	96.93	174.47	4988	9976	17859
PAHs					
Naphthalene	0.52	0.93	129.23	258.46	383.02
Acenaphthylene	0.02	0.04	6.08	12.16	21.90
Acenaphthene	0.12	0.22	8.66	17.32	27.43
Fluorene	0.32	0.57	21.52	43.04	60.38
Phenanthrene	1.07	1.93	70.21	140.42	193.79
Anthracene	0.35	0.64	3.66	7.33	13.47
Flouranthene	0.09	0.16	7.53	15.06	22.44
Pyrene	0.06	0.11	14.95	29.89	47.00
Benz(a)anthrancene	0.04	0.07	5.93	11.86	19.77
Chrysene	0.03	0.05	8.90	17.80	28.38
Benzo(b)fluoranthene	0.01	0.02	2.05	4.09	6.54
Benzo(k)fluoranthene	0.005	0.01	0.65	1.31	2.13
Benzo(a)pyrene	0.01	0.017	2.51	5.02	8.12
Dibenzo(a,h)anthracene	0.005	0.009	1.20	2.39	4.39
Benzo(g,h,i)perylene	0.005	0.009	1.12	2.24	3.88
Indeno(1,2,3-c,d)pyrene	0.004	0.007	3.43	6.86	14.52
Sum EPA 16 PAH	4.42	7.96	130.46	260.92	371.85
Sum total PAH	1.28	2.30	326.19	652.38	956.77
Nutrients					
Nitrate (NO_3^{2-})	27 744	49 939	127 550	255 100	508 970
Nitrite (NO_2^-)	13 939	25 090	34 010	68 020	149 810
Ammonium (NH_4^+)	-	-	3 290	6 570	11 020
Iron	-	-	10 830	21 660	63 517

The average discharge rate of open loop scrubbers, determined from all available data (48 measurements), is 90 m^3/MWh, twice the amount suggested by IMO (IMO 2008). This is further supported by the comparison of the different emission factors in Figure 2 and 3. Here, ship specific emission factors were calculated for those campaigns where concentrations and scrubber discharge flow rates were reported (N=48). The average and 95% confidence interval were then calculated and compared to the two open loop scenarios; $\overline{X}_i \times 45$ and $\overline{X}_i \times 90$ presented in Table 10. The results are presented in Figure 2, for metals, and Figure 3, for PAHs. The calculated ship specific emission factors coincide well and overlap with the $\overline{X}i \times 90$, supporting the statement that an average discharge flow rate of 90 m^3/MWh is more representative than the previous assumptions of using 45 m^3/MWh. Figure 2 and Figure 3 show that, using a discharge rate of 45 m^3/MWh would clearly underestimate the emission factors and thus the total load of contaminants. This further illustrates the importance of measuring and reporting the scrubber discharge flow rate at the time of sampling so that it will be possible to get a better estimate of average discharge flow rates and to calculate more accurate emission factors for future model simulations.

4.2 Grey water

As for scrubber discharge water, all raw data have been included in the Supplementary info (D.2.1.WasteStreams.xlsx) and is available for further analysis. In total, 86 onboard grey water samples have been characterized for contaminants (28 organic compounds and 16 metals/inorganic elements). However, since the main aim of EMERGE is to assess environmental impacts from scrubber discharge water, descriptive statistics of the contaminants in grey water (as well as the other waste streams) are in this report restricted to contaminants that have also been identified in scrubber discharge water. The reason behind this is that we want to have the ability to compare loads of e.g. copper from scrubber water with loads from other waste streams (grey water, sewage, antifouling paints, bilge water and ballast water). For grey water, 9 contaminants (metals) fulfilled these criteria (Table 11), were the highest concentrations where observed for zinc (517 µg/L) and copper (267 µg/L). For nutrients, the total nitrogen concentration, defined as the summary of total Kjeldal Nitrogen (the sum of ammonium and organic nitrogen) and nitrate + nitrite, was on average 28.9 mg/L. The concentration of phosphorous was lower and on average 4.8 mg/L

Table 11. Average total concentration of trace elements and metals found in grey water, presented with a 95 % confidence interval, standard deviation, number of analyzed samples (N) and percent (%) of samples below the limit of detection (LOD).

	Grey water			
	$\bar{X}$ ± 95% CI (µg/L)	Standard deviation	N	% below LOD
Arsenic	5.98 ± 3.17	11.6	51	25
Cadmium	0.16 ± 0.09	0.22	24	50
Chromium	7.28 ± 2.06	8.4	64	14
Copper	267 ± 97	413	69	0
Lead	25.6 ± 21.01	88	67	0
Mercury	0.16 ± 0.09	0.21	23	83
Nickel	25.0 ± 19.36	79.1	64	6
Selenium	16.1 ± 10.64	39.3	53	23
Zinc	517 ± 112	475	69	1

4.3 Sewage

Sewage consists of both contaminants and nutrients. In total, 16 different metals and inorganic elements and 51 different organic compounds have been identified in sewage. Out of these contaminants only 9 were also identified in scrubber discharge water (Table 12). As for greywater, zinc (395 µg/L) and copper (316 µg/L) displayed the highest concentration. For sewage, emission loads of 0.430 mg N/L and 28 mg P/L were used (Ytreberg et al. 2020).

Table 12. Average total concentration of trace elements and metals found in sewage, presented with a 95 % confidence interval, standard deviation, number of analyzed samples (N and percent (%) of samples below the limit of detection (LOD).

	Sewage			
	$\bar{X}$ ± 95% CI (µg/L)	Standard deviation	N	% below LOD
Arsenic	22.9 ± 7.4	33	77	4
Cadmium	0.12 ± 0.1	0.23	18	67
Chromium	11.9 ± 8.2	39.2	88	7
Copper	316 ± 190	944	95	0
Lead	6.5 ± 3.1	15.1	90	13
Mercury	0.22 ± 0.12	0.31	25	52
Nickel	32.3 ± 21.3	103	89	8
Selenium	43.7 ± 18.3	81.7	77	14
Zinc	395 ± 174	868	95	1

4.4 Bilge water

In bilge water, 16 different metals and inorganic compounds were identified, with 9 also present in scrubber discharge water (Table 13). In total, 36 different organic compounds, comprising oil compounds, PAHs and detergents, were identified. Of the organic compounds, 16 PAHs were also identified in scrubber discharge water and their concentrations are hence presented in Table 14.

Table 13. Average total concentration of trace elements and metals found in bilge water, presented with a 95 % confidence interval, standard deviation, number of analyzed samples (N) and percent (%) of samples below the limit of detection (LOD).

	Bilge water (Metals)			
	$\bar{X}$ ± 95% CI (µg/L)	Standard deviation	N	% below LOD
Arsenic	35.9 ± 33.2	94.4	31	48
Cadmium	0.32 ± 0.07	0.20	31	100
Chromium	16.3 ± 15.4	44.4	32	47
Copper	49.7 ± 22.9	66.2	32	19
Lead	3.0 ± 1.24	3.55	31	81
Nickel	71.1 ± 11.8	34	32	0
Selenium	2.95 ± 1.01	2.14	17	65
Vanadium	76.5 ± 22.4	64.7	32	3
Zinc	949 ± 660	1875	31	10

Table 14. Average total concentration of polycyclic aromatic hydrocarbons (PAHs) in bilge water, presented with a 95 % confidence interval, standard deviation, number of analyzed samples (n) and percent (%) of samples below the limit of detection (LOD).

	Bilge water (PAHs)			
	$\bar{X}$ ± 95% CI (µg/L)	Standard deviation	N	% below LOD
Naphtalene	50.6 ± 34.3	70.1	16	19
Acenaphtylene	0.29 ± 0.17	0.35	16	63
Acenaphtene	1.42 ± 0.86	1.76	16	38
Fluorene	3.33 ± 2.43	0.90	16	5
Phenanthrene	3.67 ± 2.51	5.12	16	38
Anthracene	0.22 ± 0.14	0.28	16	50
Fluoranthene	0.60 ± 0.96	1.95	16	31
Pyrene	1.23 ± 1.33	2.71	16	6
Benz(a)anthracene	0.10 ± 0.18	0.24	16	56
Chrysene	0.17 ± 0.25	0.52	16	38
Benz(b)fluoranthene	0.09 ± 0.13	0.27	16	75
Benz(k)fluoranthene	0.03 ± 0.00	0.07	16	94
Benz(a)pyrene	0.10 ± 0.15	0.32	16	69
Dibenzo(a,h)anthracene	0.02 ± 0.01	0.03	16	94
Benzo(g,h,i)perylene	0.13 ± 0.16	0.32	16	69
Indeno(123cd)pyrene	0.05 ± 0.06	0.14	16	81
Sum 16 PAH	61.8 ± 39.7	81.0	16	0

4.5 Ballast water

Data from 40 different BWMS have been compiled and comprises measurements of treated ballast water produced using seawater, brackish water and freshwater as medium. In total, 129 different organic compounds have been identified to be discharged from the different BWMS, none of which has been analysed in scrubber discharge water. In order to calculate the average pressure of the organic compounds to the marine environment one need to consider also the market share of the 40 BWMS in use. This was however beyond the scope of this work. Hence, Supplementary info (D.2.1.WasteStreams.xlsx) consists of characterization data per BWMS only.

4.6 Antifouling paints

Table 15. Release rates of biocides from the paint categories A – D (see section 3.6). The application rate and biocide content factor are included in the estimated release rates.

	Release rates (µg/cm²/day), per antifouling paint category			
	A	B	C	D
Copper	3.1 ± 0.9	7.5 ± 2.3	16 ± 5	25 ± 2
Zinc	1.4 ± 1.4	2.3 ± 0.7	4.6 ± 1.4	4.4 ± 1.7

4.7 Comparison of loads from different waste streams

The loads of contaminants from the model ship's different waste streams were calculated for the US EPA's 16 PAHs and the metals zinc, copper, vanadium, chromium, cadmium, nickel and arsenic. The results showed discharge water from the open loop scrubber to be the largest source of all metals investigated, including copper (Figure 4 and Table 16). The latter is somewhat alarming since emissions of copper from antifouling paints to the Baltic Sea have been estimated to be 366 tons annually (Jalkanen and Johansson 2019), which can be compared with the total annual input from all other waterborne sources (natural and anthropogenic) of 886 tons. Hence, a large-scale use of open loop scrubbers is an unregulated new waste stream that may increase the total load of copper from shipping.

PAHs were only identified in bilge water and scrubber discharge water. The results showed the loads from bilge water to be insignificant (Figure 5) whereas scrubber discharge water contributed to 99.87 – 100% of the total loads of PAHs from shipping (Table 17).

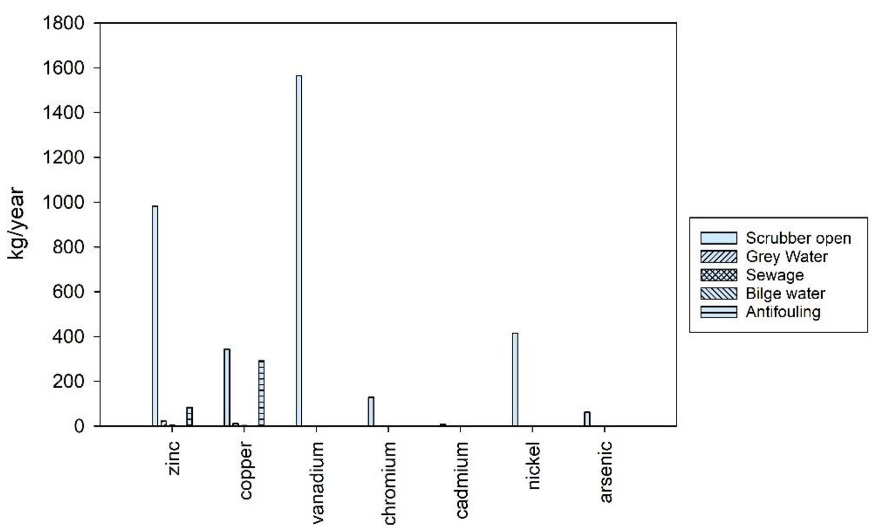

Figure 4. Yearly load of metals per waste stream from the model ship

Table 16. Proportion (in %) of metal loads from different waste streams from the model ship

	Grey Water	Sewage	Bilge water	Scrubber open	Antifouling
Zinc	2%	0%	0%	90%	8%
Copper	2%	0%	0%	53%	45%
Vanadium	0%	0%	0%	100%	0%
Chromium	0%	0%	0%	100%	0%
Cadmium	0%	0%	0%	100%	0%
Nickel	0%	0%	0%	100%	0%
Arsenic	0%	0%	0%	99%	0%

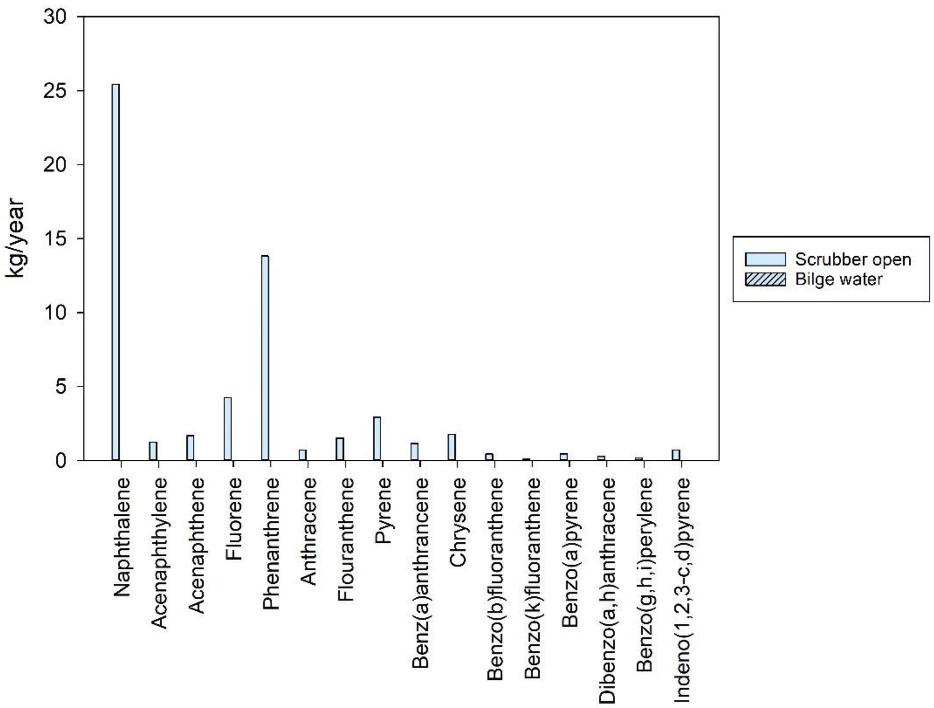

Figure 5. Yearly load of PAHs per waste stream from the model ship

Table 17. Proportion (in %) of PAHs loads from different waste streams from the model ship

	Scrubber, open loop	Bilge water
Naphtalene	99.87%	0.13%
Acenaphtylene	99.98%	0.02%
Acenaphtene	99.95%	0.05%
Fluorene	99.95%	0.05%
Phenanthrene	99.98%	0.02%
Anthracene	99.98%	0.02%
Fluoranthene	99.97%	0.03%
Pyrene	99.97%	0.03%
Benz(a)anthracene	99.99%	0.01%
Chrysene	99.99%	0.01%
Benz(b)fluoranthene	99.99%	0.01%
Benz(k)fluoranthene	99.98%	0.02%
Benz(a)pyrene	99.99%	0.01%
Dibenzo(a,h)anthracene	100.00%	0.00%
Benzo(g,h,i)perylene	99.95%	0.05%
Indeno(123cd)pyrene	100.00%	0.00%

5 Conclusions

Scrubber discharge water consists of a mixture of compounds, both organic and inorganic, with a wide range of properties and toxicities. The compounds within this complex mixture can act synergistic, enhancing and increasing the toxicity of the solution or, less common, antagonistic, reducing the toxicity. This makes it very difficult to estimate the effects of scrubbers on the marine environment. To better understand the potential cocktail effects of the scrubber discharge, in itself and when mixed with seawater and other waste loads, it is of utmost importance to characterize its composition.

There are many parameters that will influence the composition of the scrubber discharge water. When sampling on-board vessels, it is important to note the surrounding conditions so that the results may be valuated more accurately. Fuel content, discharge flow rate (or specifics that allows for calculations of the discharge flow rate) and scrubber mode of operation are examples of parameters that are paramount to include in the metadata.

This report presents new estimates on emission factors from scrubber water discharge which allow for comparison with other loads associated with shipping activity. With the available data, it is evident that assuming an average scrubber discharge flow rate of 45 m^3/MWh, as suggested by IMO, will result in an underestimation of the emission factors and thus an underestimation of the contaminant load derived from the use of scrubbers.

Measuring and reporting both particulate and dissolved fractions of contaminants is also important. Different compounds have different affinities and will thus affect different compartments of the marine environment.

The data collected in this report should be used with caution as the sampling campaigns are not always fulfilling all desired criteria. Still, the information can provide support during the initial attempts of finding substances of great concern and assessing how to mitigate the issues connected to the use of scrubbers. The variability within and between the datasets demonstrate the need for more and better data, which coincide well with the next steps within the EMERGE project.

The loads of contaminants from different waste streams from a RoPax model ship, described in section 3.7, was determined and the results showed that discharge water from open loop scrubbers are the largest source of all metals and PAHs investigated.

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