



## **Shipping and the environment: Smokestack emissions, scrubbers and unregulated oceanic consequences**

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## RESEARCH ARTICLE

# Shipping and the environment: Smokestack emissions, scrubbers and unregulated oceanic consequences

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While shipping has long been recognised as a very carbon-efficient transport medium, there is an increasing focus on its broader environmental consequences. The International Maritime Organisation is responsible for the regulation of ship emissions arising from fuel combustion. Their current regulations are, however, much less strict than those applying to land-based transport within the European Union. Five different groups of pollutant emission from ship smokestacks are addressed in this paper: sulphur oxides, nitrogen oxides, particulate matter, organic matter and metals. The reduction of sulphur oxide emissions into the atmosphere using scrubber technology adds another dimension to the discussion, as this approach results in focused discharge of some pollutants to the surface water. A scoping calculation shows that an open-loop scrubber on a medium-sized ship could discharge more copper and zinc daily to the surface water than the ship's antifouling paint. The use of antifouling paint in the European Union is subject to a prior risk assessment, but scrubber discharges are not subject to any such risk assessment. This situation presents a problem from the perspective of the Marine Strategy Framework Directive, as environmental monitoring programmes in some coastal areas of the Baltic Sea have shown that levels of both copper and zinc exceed environmental quality standards. To fulfil the Marine Strategy Framework Directive requirements and achieve Good Environmental Status, having knowledge of the magnitude of different anthropogenic pressures is important. Metal inputs from open-loop scrubbers have been largely neglected until now: some metals have the potential to serve as tracers for monitoring scrubber discharges.

**Keywords:** Shipping; scrubbers; sulphur oxides; nitrogen oxides; metals; PAH

## Introduction

The use of fossil fuels as an energy source results in the emission of a complex mixture of gases, aerosols and particulate matter to the atmosphere. Legislation to limit these emissions has been implemented both on land and at sea in order to safeguard human health and the environment. However, such legislation began to be implemented earlier for land-based emissions than for emissions from commercial shipping, and the land-based legislation continues to be more restrictive than that for shipping. We address the development of sulphur oxide scrubber technology from a marine and atmospheric environment perspective, directions for future research, and also the options for assessing the consequences of ship plumes in the context of environmental monitoring programmes.

## Regulation of ship plume emissions

The International Maritime Organisation (IMO), a body under the United Nations, has adopted the International Convention for the Prevention of Pollution from Ships (MARPOL), where Annex VI is concerned with air pollution from shipping (IMO, 2008a). This Annex regulates the emission of sulphur and nitrogen oxides ( $\text{SO}_x$  and  $\text{NO}_x$ ) from smokestacks (**Figure 1**), together with emissions of halocarbons from refrigeration plants and emissions of volatile organic compounds from oil tankers. Two levels of regulation apply for  $\text{SO}_x$  and  $\text{NO}_x$  emissions: a global level; and a stricter level applied in Emission Control Areas (ECA). The title of the  $\text{SO}_x$  regulation, no. 14 in IMO (2008a), also refers to particulate matter, but as there is no further explicit mention of particulate emissions, the emission reduction that is achieved is for sulphate aerosols only. However, extended regulation of particulate matter is under current investigation (Lack et al., 2012). Other smokestack emissions including all types of particulate matter, organic compounds such as polycyclic aromatic hydrocarbons (PAHs), and metals are not yet regulated by Annex VI. Regulation of metal concentrations in scrubber washwater has been proposed to the IMO (IMO, 2007), but the current guidelines merely state that "The wash-water treatment system should be designed to minimize

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suspended particulate matter, including heavy metals and ash" (IMO, 2008b).

#### Pollutant origin and formation

The five primary groups of pollutants in ship exhausts (Figure 1) have three major sources. The quality and type of fuel determines the amount of  $\text{SO}_x$  emitted, and also affects the emission of metals and organic matter, while lubrication fluids primarily affect metal and organic emissions. A third group of pollutants are generated during the combustion process: primarily  $\text{NO}_x$ , but also organic pollutants and particulate matter. The formation of particulate matter is complex and not yet fully understood, and is dependent on the sulphur content of the fuel (Winnes et al., 2016).

MARPOL Annex VI addresses air pollution from ships. However, a significant proportion of the emissions from ships will reach the marine environment through deposition. These processes are discussed below for each pollutant group.

#### Sulphur oxides and Sulphur Environmental Control Areas

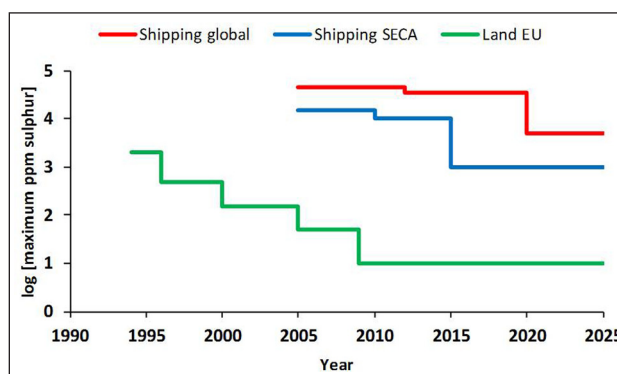
The MARPOL regulations for the maximum sulphur content of marine fuels are shown in Figure 2. The Sulphur Environmental Control Areas (SECA), where the strictest controls apply, are located in coastal seas: the only SECA in European waters covers the Baltic Sea and the North Sea. Figure 2 also shows the corresponding regulations for fuels used on land within the European Union (EU): these terrestrial regulations began to be introduced much earlier, and the differences in the current regulations are striking. The SECA regulations applying in the Baltic Sea and the North Sea allow 100 times more sulphur in marine fuel than is allowed in terrestrial fuel on the adjacent coastal land areas. Nevertheless, the reduction from 1% to 0.1% sulphur in marine fuel that took effect in January 2015 caused significant controversy because of the substantial increase in fuel costs that this sulphur reduction implied, although the subsequent fall in the oil price provided some compensation. One result has been a significant investment in the use of sulphur oxide scrubbers in the European SECA, as an economically attractive alternative to the use of expensive, low-sulphur fuel (den Boer and Hoen, 2015). Economic factors will no doubt determine whether further investments in scrubbers will occur in connection with the global limit of 0.5% sulphur, which will come into effect in 2020 (Figure 1).

#### Nitrogen oxides and Nitrogen Environmental Control Areas

Regulation of  $\text{NO}_x$  output follows a similar pattern to that of  $\text{SO}_x$ , with the significant difference that each new regulation applies to new builds only, and not to all vehicles and ships as is the case for  $\text{SO}_x$  regulations. Figure 3 shows the  $\text{NO}_x$  regulations for heavy vehicles within the EU, and the MARPOL regulations for shipping. The EU regulations for cars and other light vehicles are defined in terms of  $\text{NO}_x$  output per kilometre, and thus cannot be directly compared with the marine regulations. The MARPOL

Pollutant	Release to	
	Air	Water
$\text{SO}_x$	Green	Yellow
$\text{NO}_x$	Green	Yellow
Particulate matter	Red	Yellow
Organic pollutants	Red	Yellow
Metals	Red	Red

**Figure 1: Overview of the International Maritime Organisation's regulations and guidelines concerning ship emissions.** IMO regulations and guidelines address emissions from ship smokestacks (emission to air; IMO, 2008a) and from scrubber systems (emission to water; IMO, 2008b). Green indicates subject to IMO regulations; yellow, included in IMO guidelines; red, unregulated. DOI: <https://doi.org/10.1525/elementa.167.f1>



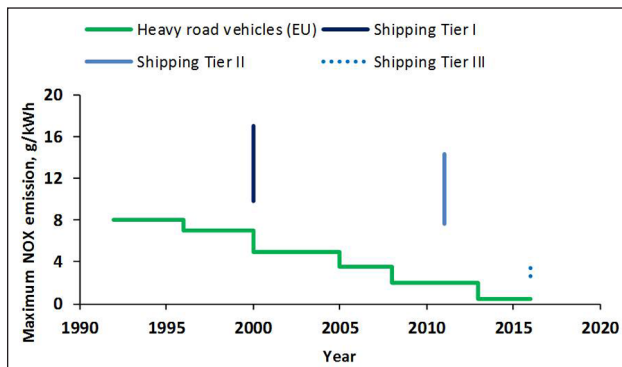
**Figure 2: The temporal development of regulations for the maximum allowed sulphur content of fuels.**

The regulations for shipping are set out in MARPOL Annex VI (IMO, 2008a) where SECA regulations apply only in Sulphur Emission Control Areas; the regulations for land transport refer to heavy vehicles in the European Union (EU, 1993, 1998, 2003). The decision to reduce the global marine fuel sulphur limit from 3.5% to 0.5% in 2020 rather than 2025 was taken very recently following a review of fuel availability (IMO, 2016). Note that the vertical scale is logarithmic. DOI: <https://doi.org/10.1525/elementa.167.f2>

regulations show a range of limits, since the limit for an individual engine is dependent on its rated speed in rpm. The marine Tier III limit, shown with a dotted vertical line in Figure 3, applies only within Nitrogen Environmental Control Areas (NECA): the only NECA currently in force is in the North America/Caribbean area, although a Baltic Sea and North Sea NECA is proposed to come into force in 2021 (HELCOM, 2016).

#### Abatement strategies

The type and origin of pollutant will call for different types of abatement strategies to meet stricter legislation regarding ship plume emissions.  $\text{NO}_x$  emissions increase with



**Figure 3: The temporal development of regulations for the maximum allowed emission of nitrogen oxides ( $\text{NO}_x$ ).** The shipping regulations (Tiers I, II and III) cover a range of allowed emissions depending on the engine's rated speed in rpm (IMO, 2008a), and are therefore shown as vertical lines in the figure. The Tier I and Tier II regulations apply to ships built from 2000 and 2011, respectively. The Tier III regulations apply only in Nitrogen Emission Control Areas for ships built from 2016. The regulations for land transport refer to heavy vehicles in the European Union (EU, 1991, 2000, 2009). DOI: <https://doi.org/10.1525/elementa.167.f3>

increased combustion temperature, and can be reduced through use of selective catalytic reduction (Flagan and Seinfeld, 1988; Brynolf et al., 2014).  $\text{SO}_x$  emissions are directly proportional to the sulphur content of the fuel and hence can be reduced by switching to an alternative fuel such as natural gas or to an oil-based fuel of lower sulphur content. In general such fuels are distilled (e.g., marine gas oil), and also cleaner with respect to other pollutants such as metals and PAHs. However, the low sulphur fuel is much more expensive and usually not compatible with the lubrication system used with heavy fuel oil. Recently however, fuel blends of marine gas oil and heavy fuel oil that comply with the 0.1% sulphur content, but avoid need for new lubrication systems, are available on the market as so-called ECA fuel (Lloyd's Register Marine, 2014). An alternative approach to meeting the  $\text{SO}_x$  emission regulations is the use of scrubbers, addressed in the next section.

#### **Emissions to water: sulphur oxide scrubbers**

While MARPOL Annex VI sets the maximum sulphur content for marine fuels, it includes the provision that fuel with higher sulphur content may be used if accompanied by an engineering solution that ensures that the  $\text{SO}_x$  content of the smokestack gases released to the atmosphere is no higher than that caused by combustion of 0.1% sulphur fuel (IMO, 2008a, 2008b). The engineering solution referred to here is the use of scrubbers, which absorb the  $\text{SO}_x$  in a fine spray of seawater. The simplest types of scrubber are "open loop" where the acidified effluent is discharged directly to the surface water (typically at a discharge rate of  $45 \text{ m}^3 \text{ MWh}^{-1}$ ; IMO, 2008b). However, most scrubbers on the market are so-called hybrid scrubbers which have the flexibility to operate in both "open

loop" and "closed loop" mode. When running in closed loop, the water is re-circulated and buffered with caustic soda. However, a minor part (approximately  $0.1$  to  $0.3 \text{ m}^3 \text{ MWh}^{-1}$ ) is discharged as so-called bleed off (IMO, 2008c). In comparison, an average sized Roll-On/Roll-Off (RoRo) vessel equipped with a 12 MW engine running on maximum load would on a daily basis produce  $13,000 \text{ m}^3$  of washwater from an open-loop scrubber. In other words, this type of scrubber reduces atmospheric pollution by redirecting (some of) the pollutants to seawater: scrubbers extract from the exhaust gases  $\text{SO}_x$ , some  $\text{NO}_x$ , and unknown proportions of organic matter, particulate material and metals. This process naturally raises the question whether the redirected acid (Kroeker et al., 2013) and pollutants such as PAHs (Pongpiachan et al., 2015) will have negative consequences for the marine environment. The development of IMO's regulatory regime has focused, however, on atmospheric pollution: while the regulations for emissions to the atmosphere are mandatory, the effluent from scrubber systems is subject only to guidelines for pH,  $\text{NO}_x$ , organic matter and particulates. These guidelines were framed as an invitation to individual member states to implement the guidelines in national legislation (IMO, 2008b).

#### **Consequences of pollutant release from smokestacks and scrubbers**

##### **Atmospheric emissions**

The near surface concentrations of smokestack pollutants as well as their deposition are focused mainly along the major shipping lanes, influencing coastal regions in particular, but pollutants released from smokestacks are also transported over longer distances (e.g. Claremar et al. (2017), Jonson et al. (2015)). Pollutant release into the atmosphere generates a variety of risks to human health, primarily to the respiratory organs and the cardiovascular system (Corbett et al., 2007). Additional consequences include the formation of ground-level ozone, and enhanced eutrophication and acidification of water and soil. Particulate matter also absorbs or reflects radiation: the net effect of emissions from the maritime sector on the global radiation balance is estimated to be negative, resulting in a cooling effect on the global climate (Eyring et al., 2005; Fuglestedt et al., 2009). Pollutant releases from smokestacks undergo transformations in the atmosphere and are deposited at the surface by dry or wet deposition. Transformation and deposition processes are dependent on turbulence, clouds and precipitation; thus the impact of smokestack release is interlinked with local meteorological conditions and atmospheric transport processes.

##### **Water quality directives**

In 2008 the EU launched the Marine Strategy Framework Directive (MSFD), an ambitious plan for efficient protection of the marine environment (EU, 2008a). The ultimate goal of the MSFD is to reach Good Environmental Status of the marine environment. To define Good Environmental Status, 11 descriptors are used, and for each descriptor a set of measurable indicators are identified. The descrip-



tors of greatest relevance for pollutant release from smokestacks and scrubbers are Contaminants (Descriptor 8) and Eutrophication (Descriptor 5).

The member states of the EU are responsible for assessing water quality, and taking measures to improve water quality where necessary. In this context it should be noted that even atmospheric emissions from shipping affect water quality via deposition of smokestack-derived pollutants. Such emissions are regulated, however, by IMO and not by the EU or its member states. As discussed above, the current IMO regulations have been developed with the aim of improving air quality, and do not address the question of water quality. The question of water quality, however, has been brought into focus by the decision of IMO to allow the use of scrubber technology in order to allow ships to comply with the MARPOL VI regulations on  $\text{SO}_x$  emissions while burning high-sulphur fuel. Through discharge of scrubber effluent, this allowance creates the potential for a new source of water pollution that lies outside the control of the EU and its member states. While limits to some components of scrubber effluent are proposed in IMO guidelines that do not have the force of law, other components such as metals can be freely discharged (**Figure 1**). We discuss below the current situation for the major pollutant groups.

#### **Sulphur oxides**

The sulphur oxides emitted to the atmosphere when using a high-sulphur fuel consist mainly of sulphur dioxide. The sulphur dioxide is then transformed into sulphuric acid resulting in acid deposition. The oxidation of  $\text{SO}_x$  to sulphate particles also forms the dominant component of shipping aerosol emissions. With the stricter regulations of land-based emissions during the last decades, ship-derived surface concentrations of  $\text{SO}_2$  approached 70% of total concentrations in some regions in the North and Baltic Sea, prior to recent regulations (Claremar et al., 2017).

The contributions of shipping to the total emissions of sulphur to the atmosphere are expected to be small in the coming decades with the present IMO regulations (e.g. (Claremar et al., 2017; Jonson et al., 2015)). However, the ongoing reductions in terrestrial sources of both  $\text{SO}_x$  and  $\text{NO}_x$  (Omstedt et al., 2015) mean that, without any accompanying regulation of emissions from shipping, one can expect a relatively significant proportion of a smaller total acid deposition into the North Sea and Baltic Sea to originate from shipping smokestack emissions.

#### **Nitrogen oxides**

Nitrogen oxides include nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ), which are emitted from fuel combustion processes. Following oxidation and deposition, these oxides contribute the plant nutrient nitrate to the surface water. Presently, critical loads for eutrophication are exceeded throughout most of the land areas around the Baltic Sea and the North Sea (Gauss et al., 2013), with a significant fraction of the nitrogen depositions originating from shipping (Jonson et al., 2015). Besides adding to acidification and eutrophication in the Baltic Sea and North Sea, nitrogen oxides emitted into the atmosphere,

in common with carbon monoxide and volatile organic compounds, react in the presence of sunlight forming tropospheric ozone. The MARPOL guidelines for the release of scrubber effluent require that the scrubber takes up no more than 12% of the  $\text{NO}_x$  in the smokestack gases (IMO, 2008b). This provision is intended to limit the discharge of excess nitrate to surface waters, a particular concern in coastal waters suffering from eutrophication. The uptake of  $\text{NO}_x$  in a scrubber depends on the exhaust gas ratio between nitric oxide (NO, poorly soluble in water) and nitrogen dioxide ( $\text{NO}_2$ , which reacts quickly with water to form nitrous and nitric acids). The  $\text{NO}_x$  uptake limit is thus in effect a limit to the proportion of soluble  $\text{NO}_2$  in the total  $\text{NO}_x$ .

#### **Particulate matter**

Particulate matter from shipping consists of a complex mixture of soot, sulphate, metals and other organic and inorganic fragments (Winnes et al., 2016). The prime component is, however, sulphate formed by oxidation (Eyring et al., 2010). The quantity and size of particulate matter depends mainly on the type of fuel and its sulphur content, as well as the ship's engine (Fridell et al., 2008; Aardenne et al., 2013). Using wet scrubbers will most likely reduce the emissions of particles into the atmosphere (Winnes et al., 2016), but also alter their physical and chemical properties. Scrubbers also influence the micro- and nano-structural characteristics of the particles (Lieke et al., 2013) as well as their size distribution.

#### **Organic pollutants**

The organic pollutants of greatest concern are PAHs, which are largely associated with small-sized particulate matter. There are few studies of the effect of smokestack emissions on atmospheric PAH concentrations: Contini et al. (2011) reported that shipping contributed 10% of atmospheric PAH in Venice, while Pongpiachan et al. (2015) reported from a study in Thailand that the genotoxicity of atmospheric particles from shipping emissions was higher than for other sources, and was associated with higher PAH concentrations. It has been argued that because most PAHs are particle-bound, scrubbers can play a positive role by reducing the particulate content of the smokestack emissions (IMO, 2006). Both atmospheric deposition and scrubber water discharge can result in the accumulation of particle-bound PAHs in sediments. Studies of PAH composition in coastal and inland water sediments indicate potentially harmful levels at some sites, but source identification based on PAH composition is unable to distinguish shipping from other sources using similar fuels (Hu et al., 2011; Wang et al., 2012; Guo et al., 2013; Sany et al., 2014; Zheng et al., 2015).

#### **Metals**

Although only limited data are currently available, monitoring conducted on discharge water from open-loop scrubbers indicates concentrations well above the Predicted No-Effect Concentration values for both copper and zinc used in risk assessments in the EU (2.6 and 7.8  $\mu\text{g L}^{-1}$ , respectively; SCHER, 2007; EU, 2008b). The highest total

copper and zinc concentrations reported in discharge water are 260 and 537  $\mu\text{g L}^{-1}$ , respectively (**Table 1**). In total, 18 discharge waters have been analysed for metal concentrations and the average concentrations of copper and zinc are 60 and 136  $\mu\text{g L}^{-1}$ , respectively (**Table 1**). Thus, the average daily load of copper and zinc from a medium-sized RoRo vessel equipped with a 12 MW main engine would be 780 g Cu and 1770 g Zn. This calculation assumes maximum engine load and that the discharge water concentrations of copper and zinc are 60 and 136  $\mu\text{g L}^{-1}$  respectively, and that the discharge rate is 45  $\text{m}^3 \text{MWh}^{-1}$ . To put the scrubber emissions into a larger context, the daily load from a typical copper- and zinc-containing antifouling paint was determined. The release rates of a typical copper-based paint (Interspeed 5617) are 8.11 and 2.2  $\mu\text{g cm}^{-2} \text{d}^{-1}$  for copper and zinc, respectively (Annelie Rudström, Swedish Chemicals Agency, personal communication). According to Endresen and Sorgård (1999), the wetted surface area of an average RoRo vessel is 3817  $\text{m}^2$ . This example will result in a daily discharge of 310 g  $\text{d}^{-1}$  of copper and 84 g  $\text{d}^{-1}$  of zinc from the antifouling paint; the

estimated scrubber discharges are thus 2.5 and 21 times higher than the releases from antifouling paint for copper and zinc, respectively.

Within the EU, antifouling paints are regulated through the Biocidal Product Regulation (BPR 528/2012). The regulation implies that all paints have to pass an environmental risk assessment (ERA) prior to being put out on the market. In the ERA process, national authorities review the application to assess whether the use of the antifouling product poses an acceptable risk to the marine environment. In contrast to antifouling paints, no ERA is required for scrubbers, although proposals in this regard have been submitted to IMO (IMO, 2006, 2007). This discrepancy in risk assessment requirements is unfortunate, as recent Swedish environmental monitoring programmes in the Stockholm Archipelago (Österås and Allmyr, 2015) have shown both dissolved copper and zinc concentrations at many sites to be above the water quality criteria for the Baltic Sea (i.e.,  $>1.45 \mu\text{g L}^{-1}$  for copper and  $>1.1 \mu\text{g L}^{-1}$  for zinc; SWAM, 2013). The use of open-loop scrubbers may therefore be in direct conflict with the requirement for

**Table 1:** Reported copper and zinc concentrations in open-loop scrubber discharge water. DOI: <https://doi.org/10.1525/elementa.167.t1>

Vessel	Scrubber installation <sup>a</sup>	Cu ( $\mu\text{g L}^{-1}$ )	Zn ( $\mu\text{g L}^{-1}$ )	V ( $\mu\text{g L}^{-1}$ )	References
<i>Pride of Kent</i> (RoRo <sup>a</sup> )	AE	129 <sup>b</sup>	537 <sup>b</sup>	0	(Hufnagl et al., 2005)
	AE	0 <sup>b</sup>	290 <sup>b</sup>	0	
	AE	48 <sup>b</sup>	147 <sup>b</sup>	29	
	AE	0 <sup>b</sup>	0 <sup>b</sup>	0	
	AE	0 <sup>b</sup>	0 <sup>b</sup>	0	
	AE	48	229	0	
	AE	0 <sup>b</sup>	138 <sup>b</sup>	0	
	AE	0 <sup>b</sup>	0 <sup>b</sup>	0	
	AE	32 <sup>b</sup>	96 <sup>b</sup>	0	
<i>Ficaria</i> (RoRo)	ME	260 <sup>c</sup>	450 <sup>c</sup>	180	(Kjølholt et al., 2012)
	ME	150 <sup>c</sup>	150 <sup>c</sup>	81	
	ME	110 <sup>c</sup>	110 <sup>c</sup>	49	
	ME	150 <sup>c</sup>	98 <sup>c</sup>	25	
	ME	82.2 <sup>b,d</sup>	40.2 <sup>b,d</sup>	104	
<i>Magnolia Seaways</i> (RoRo)	ME	6.9 <sup>b,d</sup>	5.2 <sup>b,d</sup>	96	This work
<i>Fjordshell</i> (tanker)	ME	41.6 <sup>e</sup>	6 <sup>e</sup>	N/A <sup>f</sup>	(Buhaug et al., 2006)
	ME	15.3 <sup>e</sup>	15 <sup>e</sup>	N/A	
<i>Zaandam</i> (passenger)	ME	15 <sup>b,g</sup>	N/A	N/A	(USEPA, 2011)

<sup>a</sup> Installed on either the auxiliary engine (AE) or the main engine (ME) of Roll-On/Roll-Off (RoRo), tanker and passenger ships.

<sup>b</sup> Filtered ( $<0.45 \mu\text{m}$ ) concentrations.

<sup>c</sup> Total concentrations.

<sup>d</sup> Metal analysis performed by ALS Scandinavia AB, Sweden, using Inductively Coupled Plasma Sector Field Mass Spectrometry according to EPA method 200.8 rev5.4 (1994) and SS EN ISO 17294-1 (2006).

<sup>e</sup> Not specified if concentrations refer to filtered or total metal concentrations.

<sup>f</sup> N/A = not available.

<sup>g</sup> Median concentration ( $n = 7$ ).

measures to be taken to decrease the dissolved copper and zinc concentrations in order to fulfil Good Environmental Status according to Descriptor 8 under the MSFD.

As emphasised in several reports on scrubber discharge water, the origin of copper and zinc in the scrubber water is unknown (Hufnagl et al., 2005; Kjølholt et al., 2012). Potential metal sources may include combustion of fuel and lubricants. However, combustion of fuel is most likely not a significant source, as Kjølholt et al. (2012) showed that the concentration of both copper and zinc in the heavy fuel oil used on board the vessel *Ficaria* was below the limit of quantification ( $<3$  and  $20 \text{ mg kg}^{-1}$ , respectively). Other potential sources include the use of impressed current cathodic protection systems in the sea chest, which operate by releasing copper ions that are carried through the cooling system. Another source of metals can be the piping material of the seawater cooling system and of the scrubber system itself. In a study conducted by the US Navy and the US Environmental Protection Agency (USEPA and USDOD, 1999), the mean concentration of copper in the cooling water discharge water from five US Navy ships was reported as  $34.5 \text{ } \mu\text{g L}^{-1}$ .

The metal content of smokestack gases has also received attention, with particular emphasis on vanadium and nickel, which are known to occur in heavy fuel oil and therefore could act as tracers for smokestack emissions (see next section). However, the metal which could have a significant impact on oceanic ecosystems is iron. A study by Ito (2013) notes that the seawater solubility of particulate iron produced from oil combustion is significantly higher than for other iron-containing aerosols. This modelling study concluded that shipping may contribute around 40% of the soluble iron deposition to the northeastern Pacific Ocean, one of the world's High Nutrient Low Chlorophyll areas where photosynthesis is limited by the low iron concentrations. A long-term simulation in the same paper concluded that shipping emissions could contribute 30–60% of the soluble iron deposition to the North Atlantic and North Pacific oceans by the year 2100. While changes in fuel choice and fuel quality may well reduce this contribution, the study stands as a warning that shipping emissions can have significant consequences even on the scale of a major ocean basin.

### Monitoring of ship plumes and scrubbers

While the consequences of scrubber operation in both the short and long term are the focus of continuing research, it is worthwhile to consider whether the resulting changes to the water chemistry can be followed in the framework of environmental monitoring programmes. While the initial focus has been on the acidifying effect of the  $\text{SO}_x$  and  $\text{NO}_x$  emissions (Hunter et al., 2011; Hassellöv et al., 2013; Hagens et al., 2014), it has become clear that the effects on pH on a basin scale are limited (Hunter et al., 2011; Omstedt et al., 2015). However, a high resolution North Sea modelling study has confirmed that the largest effects are found close to heavily trafficked harbours, where the pH change can equal that due to increased uptake of  $\text{CO}_2$  from the atmosphere (Stips et al., 2016). This finding

may provide a monitoring potential in heavily trafficked areas. The reduction of alkalinity through the deposition of strong acids is also a potential monitoring option, but would need to assume an otherwise constant alkalinity. This assumption may not always be true: for example, a recent study has shown that the alkalinity of the Baltic Sea is increasing, presumed due to changes in runoff (Müller et al., 2016). A more promising option for monitoring the releases due to combustion of heavy fuel oil may be the metal vanadium. Zhao et al. (2013) noted that nickel has a range of sources, while shipping was considered to be the prime source of vanadium in atmospheric particulate matter. These authors used vanadium concentrations to trace the contribution of shipping to atmospheric particulate matter in the Shanghai port area. The vanadium concentrations in scrubber washwater reported in **Table 1** have a geometric mean and median of  $84$  and  $96 \text{ } \mu\text{g L}^{-1}$ , respectively, which are 47 and 54 times higher than the vanadium concentration naturally present in seawater, ca.  $35 \text{ nmol kg}^{-1}$  (Jeandel et al., 1987). Modelling studies would be needed to determine whether these differences are large enough to make vanadium an attractive tracer option.

### Conclusions

Smokestack emissions from shipping are currently more lightly regulated than the corresponding terrestrial emissions within the European Union. There is, however, an ongoing process in strengthening regulations in selected control areas as well as globally. This process has accelerated the use of scrubber technology to reduce sulphur oxide emissions while burning high-sulphur fuel and has added another dimension in the form of the direct discharge of pollutants to the water column. The washwater discharges are subject only to advisory guidelines, currently only with respect to pH,  $\text{NO}_x$ , turbidity and PAH, i.e., not encompassing metal content. This situation is unfortunate, as the potential environmental impact of metal release, especially during acidic conditions, may actually pose a more severe threat from scrubbers than the pollutant groups today included in the guidelines, reflecting a new problem arising. Scrubber regulations are constructed from an 'emissions to air perspective'; while focusing on the reduction of emissions to air, the resulting discharge to water is not adequately handled in terms of harmonisation with the MSFD. Thereby scrubber discharge water is not subject to the prior Environmental Risk Assessment that is normally required for potentially polluting discharges within the European Union.

### Data Accessibility Statement

The only data generated in this work are the metal concentrations reported in Table 1.

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### Competing interests

The authors have no competing interests to declare.

### Author contributions

- Contributed to conception and design: DRT, I-MH
- Contributed to acquisition of data: EY
- Contributed to analysis and interpretation of data: DRT, I-MH, AR, EY
- Drafted and/or revised the article: DRT, I-MH, AR, EY
- Approved the submitted version for publication: DRT, I-MH, AR, EY

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