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Dry bulk cargo shipping — An overlooked threat to the marine environment?



Matthias Grote ^{a,*}, Nicole Mazurek ^a, Carolin Gräbsch ^a, Jana Zeilinger ^b, Stéphane Le Floch ^c, Dierk-Steffen Wahrendorf ^d, Thomas Höfer ^a

^a Federal Institute for Risk Assessment (BfR), Unit Transport of Dangerous Goods, Max-Dohrn-Straße 8-10, 10589 Berlin, Germany

^b bluetox, Gartenstraße 27, 24103 Kiel, Germany

^c Centre de documentation, de recherche et d'expérimentations sur les pollutions accidentelles des eaux (Cedre), Rue Alain Colas/CS 41836, 29218 Brest, Cedex 2, France

^d German Federal Institute of Hydrology (BfG), Am Mainzer Tor 1, 56068 Koblenz, Germany

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ABSTRACT

Approximately 9.5 billion tonnes of goods is transported over the world oceans annually with dry bulk representing the largest cargo group. This paper aims to analyse whether the transport and associated inputs of dry bulks into the sea create a risk for the marine environment. For this purpose, we analyse the international regulatory background concerning environmental protection (MARPOL), estimate quantities and identify inputs of such cargoes into the oceans (accidental and operational), and use available information for hazard assessment. Annually, more than 2.15 million tonnes of dry bulk cargoes are likely to enter the oceans, of which 100,000 tonnes are potentially harmful to the marine environment according to the definition included in draft maritime regulation. The assessment of the threat to the marine environment is hampered by a lack of available information on chemical composition, bioavailability and toxicity. Perspectives for amendments of the unsatisfying pollution prevention regulations are discussed.

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1. Introduction

Maritime transport is the backbone of the World Economy. It is generally believed that more than 90% of world trade is carried by sea (Tsaini, 2011). In 2013, approximately 9.5 billion tonnes of goods was loaded for seaborne transport in ports worldwide (UNCTAD, 2014), which can be divided into 3 main cargo groups: containers, liquid bulk cargo (or "wet" trades such as crude oil, petroleum products and gas) and solid bulk cargo (or "dry" trades such as coal, iron ore and grain). Each of these cargo groups requires special vessels: container ships, tankers and bulkers respectively. In terms of volumes, dry bulk cargoes represent the largest group accounting for more than 50% of all loaded goods (30% for liquid bulk cargoes, and 16% for containers) (UNCTAD, 2014). Overall, mineral oils and solid bulks constitute the largest homogenous shipment volumes on board single ships. Vessels carrying about 100,000 tonnes of such cargoes are quite common in maritime transport.

In the 1960s, accidental spills of oils caused the contamination of coasts and death of thousands of sea birds. The media coverage of these events drew public attention to environmental hazards of mineral

* Corresponding author. *E-mail address:* matthias.grote@bfr.bund.de (M. Grote). oil transport and triggered the *International Convention for the Prevention of Pollution from Ships* (MARPOL). However, it was not before 2011 that the potential environmental impacts of dry bulk cargoes were noted on the regulatory level by the delegates meeting at the Marine Environment Protection Committee (MEPC) of the International Maritime Organization (IMO). It was noted during the discussions with ship owners that it was a common practice to wash overboard cargo residues left on bulkers after unloading. With the amendment of the Annex V of MARPOL in 2012, discharge of cargo residues, which are harmful to the marine environment, is forbidden from 2015.

This paper aims to analyse for screening purposes whether the transport and the associated input of dry bulk cargoes into the marine environment represent a risk for the marine environment including human health. More specifically the present paper aims:

- to give an overview of the international regulatory background concerning environmental and health risks linked to the transport of dry bulks;
- to provide available data for quantification of accidental and operational inputs of dry bulks into the marine environment;
- to assess available information allowing hazard assessment for bulk cargo commodities and resulting legal classification / restrictions concerning dumping;

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- to identify further information requirements and to develop a more appropriate approach for an improved regulation.

2. Overview of regulations concerning marine environmental protection

2.1. SOLAS

The IMO is the specialised agency of the United Nations dealing with safety of shipping, navigation and the reduction and prevention of marine pollution from ships. One of its first major achievements was the *International Convention for the Safety of Life at Sea* (SOLAS) which entered into force in 1965 and which aims to ensure that ships comply with minimum safety standards in construction, equipment and operation.

2.2. IMSBC code

With respect to the safety of dry goods transported in bulk, SOLAS refers to the mandatory *International Maritime Solid Bulk Cargoes Code* (IMSBC Code) which provides information on the dangers associated with the shipment of different types of solid bulk cargoes (except grain). The code lists typical products (see Table S1) which are shipped in bulk (named schedules), gives instructions on the appropriate safety procedures (stowage requirements, maximal moisture content etc.) and describes various test procedures which should be employed to determine the characteristic cargo properties. In its 2013 edition (IMO, 2013), which became mandatory from 1 January 2015, 168 individual schedules of solid bulk cargoes are listed and described. However, wheat, corn, oats, rye, barley, rice, pulses, seeds and the processed forms of these grains are regulated by the International Grain Code.

2.3. MARPOL

Environmental issues have been addressed by the IMO since the early 1970s. The *International Convention for the Prevention of Pollution from Ships* (MARPOL), signed in 1973, is one of the most important international marine environmental conventions. It aims at protecting the marine environment through the minimisation or complete elimination of pollution by oil and other harmful substances. It is constantly updated in order to tackle new aspects of environmental pollution, which is performed by amendments and annexes to the convention.

2.4. MARPOL Annex V

Today, MARPOL contains six annexes addressing the prevention of several types of pollution. For different reasons, no individual annex for solid bulk cargoes was drafted, but it is considered that the rules for garbage discharge (addressed in Annex V) apply, which aim at zero-level pollution and restrict any dumping of garbage. However, it was noted during discussions at the IMO that although forbidden it was a common practice to wash overboard cargo residues left on bulkers after unloading. According to information from shippers, these "residues" can represent discharges of 60 tonnes of washing slurry per hold and even more during routine procedures on board dry bulk carriers. For this reason, the MEPC of the IMO felt the need to establish clearer rules on the regulatory level and reviewed the MARPOL Annex V in 2011 in order to better deal with the potential environmental impacts of dry bulk cargoes.

2.5. MARPOL Annex V guideline

A guideline regulating the discharge of cargo residues from solid bulk carriers (IMO, 2012a) was drafted, which defines criteria for solid material considered as *Harmful to the Marine Environment* (HME) based on the United Nations Globally Harmonized System for Classification and Labelling of Chemicals (GHS) (United Nations, 2015). According to the MARPOL Annex V guideline, cargoes meeting one or more of the following criteria are considered HME:

In brief, criterion 1 comprises compounds inducing acute (short-

- 1. Acute aquatic toxicity category 1
- 2. Chronic aquatic toxicity category 1 or 2
- 3. Carcinogenicity^a category 1A or 1B
- 4. Mutagenicity^a category 1A or 1B
- Reproductive^a toxicity category 1A or 1B
 Specific target organ toxicity^a repeated
- exposure category 1
- when combined with not being rapidly degradable and having high bioaccumulation^b
- Solid bulk cargoes containing or consisting of synthetic polymers, rubber, plastics, or plastic feedstock pellets (this includes materials that are shredded, milled, chopped or macerated or similar materials).

^a Products that are classified for carcinogenicity, mutagenicity, reproductive toxicity or specific target organ toxicity repeated exposure for oral and dermal hazards or without specification of the exposure route in the hazard statement (i.e. excluding inhalation hazards).

^b According to GHS criteria, the potential to bioaccumulate concerns compounds with an experimental bioconcentration factor (BCF) \geq 500 or a log $K_{OW} \geq 4$.

term) toxic effects in aquatic organisms (fish, crustacea and algae) in concentrations $\leq 1 \text{ mg/L}$ (i.e. LC50/EC50 $\leq 1 \text{ mg/L}$). Criterion 2 comprises compounds inducing chronic (long-term) toxic effects in concentrations $\leq 0.1 \text{ mg/L}$ (if non-rapidly degradable) or $\leq 0.01 \text{ mg/L}$ (if rapidly degradable) (i.e. NOEC $\leq 0.1 \text{ mg/L resp.} \leq 0.01 \text{ mg/L}$). If no chronic test data are available and the compound is not rapidly degradable or the bioconcentration factor is \geq 500, criterion 2 also covers acutely toxic compounds (LC50/EC50 \leq 10 mg/L). Criteria 3 to 6 include bioaccumulating and not rapidly degradable compounds being carcinogenic, mutagenic and/or reprotoxic (CMR) in mammals or exhibiting significant specific target organ toxicity (STOT) in mammals. Furthermore, criterion 7 addresses polymers and plastics without reference to specific hazard classes. The rationale behind these criteria is based on the objectives of the MARPOL convention which aims to protect marine life from toxic effects and litter, and to protect human health, which might be exposed to pollutants via the consumption of seafood.

With the final approval of the non-mandatory guideline regulating the discharge of cargo residues from solid bulk carriers (IMO, 2012a), cargo residues not classified as Hazardous to the Marine Environment are exempted from most discharge restrictions and may be discharged everywhere into the sea *en route* at a distance of at least 12 nautical miles from coast). Discharge of HME classified cargoes is restricted. From 1 January 2015, implementation of the non-legally binding rules should be applied. In 2016, the environmental committee of IMO (MEPC) decided to make the criteria for classification of harmful solid bulk cargoes mandatory in the future.

The approach taken by the IMO is purely based on compound specific hazards. The criteria were decided without any estimation of the impact on the operation procedures on board bulkers and without any official scientific risk evaluation by e.g. independent United Nations' experts. IMO sensibly chose 'intrinsic properties' as the basis of most of its regulation, because the data for risk assessment are not expected to become sufficient.

3. Cargoes

According to data from the United Nation Conference on Trade and Development (UNCTAD), 4.3 billion tonnes of dry bulk cargoes (i.e. commodity cargo that is transported unpackaged in large quantities in granular, particulate form) were shipped in 2013. Dry bulks represent approximately 54% of the shipping volumes worldwide (UNCTAD, 2014). The five major bulk commodities (iron ore, coal, grain, bauxite/ alumina and phosphate rock) account for about 57% of total volume of all transported dry bulk commodities (UNCTAD, 2014). However, a large range of other dry bulk commodities is shipped. The IMSBC Code, which applies to all solid bulk cargoes except grain currently lists 168 bulk commodities. No clear criteria for definition of cargo types are provided. The number of distinct goods is higher than 168 as many schedules assign group entries with rather unspecific (chemical)

characteristics. Some schedules denote large rather imprecise or heterogeneous groups of goods. Especially the schedule "mineral concentrates" lists 24 more specific bulk cargo shipping names, including copper, lead, manganese, nickel and zinc concentrates. A detailed list of schedules listed in the 2013 version of the IMSBC Code can be found in the supplementary information (Table S1), on which our

Table 1

Potential candidates for cargoes regulated under MARPOL Annex V as hazardous to the marine environment (HME).

		Ecotoxicity (covering MARPOL criteria 1 and 2)		Human health (covering MARPOL criteria 3 to 6)					eria 3 to 6)
Bulk cargo shipping name (IMSBC Code)	Constituents (bold according to MARPOL V potentially relevant for HME classification)	Aquatic to	oxicity	С	М	R	STOT	Bioacc	Not rapidly degradable
		Acute	Chronic	≥0.1%	≥0.1%	≥0.1%	≥1%		0
Chopped rubber and plastic insulation		Cargo con classified	tain synthe as HME und	tic polyr ler MAR	ners, rul POL Anr	bber, or nex V	plastic	feedstoc	k pellets =
Coal tar pitch	Primarily 3 to 40 ringed polynuclear aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAH), C20–28	\mathbf{x}_{PAH}	\mathbf{x}_{PAH}	\mathbf{x}_{PAH}	\mathbf{x}_{PAH}	\mathbf{x}_{PAH}		х	х
Coarse chopped tyres		Cargo con classified	tain synthe as HME und	tic polyr ler MAR	ners, rul POL Anr	bber, or nex V	plastic	feedstoc	k pellets =
Copper granules	Copper (75%) and others: lead, zinc	X _{Cu, Pb, Zn}	X _{Cu, Pb, Zn}			\mathbf{x}_{Pb}		х	х
Copper matte	Copper (45–75%), lead sulphide (0.3–7.5%) , nickel (≈1%)	X _{Cu, PbS}	X _{Cu, PbS}			X _{PbS}		х	х
Crushed carbon anodes	Carbon, trisodium hexafluoroaluminate (cryolite) (0–5%) , aluminium oxide						х	?	х
Cryolite	Carbon, trisodium hexafluoroaluminate (cryolite) , aluminium oxide		х				х	?	х
Ferrophosphorus	Chromium, iron, manganese, phosphorus, silicon, titanium, vanadium (pentoxide) (≤0.6%) , zinc (1–4.5%) ; after contact with water may evolve phosphine (PH3)	X _{PH3, Zn}	X _{Zn, V205}						х
Ferrosilicone	Ferrosilicon, iron silicide, iron discilicide, silicon, iron, aluminium, carbon, Phosphorus; after contact with water may evolve phosphine (PH3) and arsine (AsH3)	XpH3, AsH3	X _{AsH3}						х
Granulated nickel matte	Arsenic (0.2%), cobalt sulphide (\leq 1%), copper (9%), iron, nickel sulphide (60, 80%), zinc (<0.01)	X _{As, CoS,}	X _{As, CoS,}					х	х
Granulated tyre rubber	Supine (00-00%), 2inc (~0.01)	Cu, Nis Cargo con classified	tain synthe as HME unc	tic polyr ler MAR	ners, rul POL Anr	bber, or nex V	plastic	feedstoc	k pellets =
Lead Nitrate UN 1469	Lead nitrate	х	х			х	х	х	х
Lead Ore	Arsenic (≤0.5%), copper (indefinite), iron, lead and lead sulphide (50–70%), silicon, zinc (13–18%)	X _{As, Cu,} PbS, Zn	X _{As, Cu,} PbS, Zn	\mathbf{x}_{As}		\mathbf{X}_{PbS}		х	х
Manganese ore	Aluminium oxide, barium oxide, iron oxide, manganese oxides (trimangantetraoxide, mangandioxide), quartz; lead , copper , zinc (<1%)	X _{Cu, Pb, Zn}	X _{Cu, Pb, Zn}			x _{Pb}		х	х
Metal sulphide concentrates	e.g. zinc concentrate, lead concentrate, copper concentrate:	X _{CuS, CdS,}	X _{CuS, CdS,}	X _{CdS}		X _{PbS}	X _{CdS}	х	х
Mineral Concentrates	cadmium sulphide, copper sulphide, copper iron disulphide,	NiS, PbS	NiS, PbS						
Pellets (concentrates)	iron sulphide, lead sulphide, nickel sulphide, zinc sulphide								
Nickel ore	Oxides of: aluminium, cobalt , iron, nickel , silicates: aluminium, iron, magnesium	X _{NiS, CoO}	X _{NiS, CoO}					х	х
Pitch prill	Benzo[a]pyrene			х				х	х
Pyrites (uncalcined)	Arsenic (9%) , iron sulphide, lead , zinc (1%) , quarz (see mineral concentrate)	X _{As, Zn}	x _{As, Zn}	\mathbf{x}_{As}		x _{Pb}		х	х
Silicomanganese	Carbon, chromium, iron, manganese, nickel, phosphorus, silicon; after contact with water may evolve phosphine and arsine	X _{PH3, AsH3}	X _{AsH3}						х
Solidified fuel recycled from paper and plastics		Cargo con classified	tain synthe	tic polyr ler MAR	ners, rul POL Anr	bber, or nex V	plastic	feedstoc	k pellets =
Vanadium ore	Lead, vanadium, vanadium oxides, zinc	X7n	X7n V205			Хрь		х	х
Zinc ashes	Zinc oxide	X	X			**r0		x	x

Acute aquatic toxicity: 96 h LC50 (for fish), 48 h EC50 (for crustacea), or 72 or 96 h ErC50 (for algae or other aquatic plants) ≤ 1 mg/L.

Chronic aquatic toxicity: (i) chronic NOEC or ECx (for fish, crustacea, algae, or other aquatic plant) \leq 0.1 mg/L for rapidly degrading compounds, or (ii) acute LC/EC50 values \leq 10 mg/L if no chronic test data are available and the compound is not rapidly degradable or the bioconcentration factor is \geq 500.

C; carcinogenic: substances known or presumed to have carcinogenic potential for humans according to Fig. 3.6.1 of the GHS and Table 3.6.1 of the GHS in respect to the concentration limit of $\geq 0.1\%$ triggering classification of mixtures (see United Nations, 2015; GHS Chapter 3.6).

M; mutagenic: substances known to induce heritable mutations in germ cells of humans or which should be regarded as if they induce heritable mutations in the germ cells of humans according to Fig. 3.5.1 of the GHS and Table 3.5.1 of the GHS in respect to the concentration limit of $\geq 0.1\%$ triggering classification of mixtures (see United Nations, 2015; GHS Chapter 3.5). **R**; reprotoxic: substances known or presumed to be a reproductive toxicant according to Fig. 3.7.1(a) of the GHS and Table 3.7.1 of the GHS in respect to the concentration limit of $\geq 0.1\%$ triggering classification of mixtures (see United Nations, 2015; GHS Chapter 3.7).

STOT; specific target organ toxicity repeated exposure: substances that have produced significant toxicity in humans, or that, on the basis of evidence from studies in experimental animals can be presumed to have the potential to produce significant toxicity in humans following repeated exposure according to Fig. 3.9.1 of the GHS and Table 3.9.3 of the GHS in respect to the concentration limit of \geq 1% triggering classification of mixtures (see United Nations, 2015; GHS Chapter 3.9).

Bioacc (bioaccumulating): substances showing a potential to bioaccumulate with a bioconcentration factor of \geq 500. Note: This property is no separate building block in the GHS and used here in analogy to paragraph 4.1.2.10 of the GHS (see United Nations, 2015; GHS Chapter 4.1).

Not rapidly degradable: lack of rapid degradability is based on either a lack of ready biodegradability or other evidence of lack of rapid degradation. When no useful data on degradability are available, either experimentally determined or estimated data, the substance is regarded as not rapidly degradable. Note: This property is no separate building block in the GHS and used here in analogy to Table 4.1.1 footnote 4 and paragraphs 4.1.2.11 and 4.1.2.12 of the GHS (see United Nations, 2015; GHS Chapter 4.1).

X: classified according to the criteria of the respective column criteria with additional subscript identification of the specific cargo/mixture component asking for classification.

analysis is based. However, although handled and shipped in large quantities, little to any information concerning shipped volumes of specific minor bulks are publicly available.

4. Hazard identification

One part of this study was to identify those cargoes which are potentially Hazardous to the Marine Environment (HME) according to the IMO regulation. As a starting point, we focussed on the 168 cargo schedules listed in the 2013 version of the IMSBC Code. We noticed a significant and general deficit in availability of hazard data and material safety data sheets within the maritime solid bulk cargo business. This might be due to the fact that this information was not systematically required prior to the implementation of the Annex V guideline and the fact that ores, waste and similar bulk commodities are in general exempted from the European chemical legislation REACH.

We tried to identify the chemical composition of the 168 "schedules" in the IMSBC Code (c.f. Table S1). Based on the chemical components, studies on potential environmental and health hazards as well as hazard classification data were retrieved from public databases inter alia including OECD's eChemPortal, databases at the European Chemical Agency (ECHA), US Environmental Protection Agency (EPA) Ecotox Database and hazard ratings by the GESAMP Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships (IMO, 2012b). The hazard identification was based on legal classification of identified components. The majority of documents were assessment reports, and hazard classifications developed by the industry for the industry. In many cases no detailed scientific study reports were available. All these had in common that they were "secondary data" based on evaluations of test reports or sometimes even scientific estimations. However, some high quality reports from North-American or European agencies or international organizations (e.g. OECD) on specific mixtures or components became available that could be trusted in their assessments.

For each schedule, we tried to identify potential hazardous components with a concentration range and assigned associated hazard codes according to the GHS criteria. For minerals, the assessment had to be based on the ionic form of the components as the specific data of the inorganic components (heterogeneous mineral structures with differences in solubility and bioavailability) were in general not available. This approach assumes a high bioavailability, which may be an overestimation in some cases (this aspect is addressed under section discussion). The hazard assessment of relevant components was used for classification of the cargo as no detailed mixture calculation could be performed because there were no clear data on composition.

Schedules covering products (cargoes) listed in Table 1 potentially meet the criteria of MARPOL Annex V and therefore may have to be classified as HME. These include several ores or alloys containing high amounts of arsenic, cadmium, copper, lead, nickel and/or zinc, but also all bulks consisting of chopped or ground plastics or rubber (criterion 7) and pitch prill, which contains high amounts of polycyclic aromatic hydrocarbons (PAHs).

For a number of bulk schedules, a clear classification was not possible. This is due to some bulk cargo names within the IMSBC Code covering cargoes with ambiguous composition, which do not even allow a rough estimate of its chemical constitution and consequently its toxicological and ecotoxicological characteristics (see Table S1 in supplementary material: Bulk cargo names with an asterisk). Furthermore, it has to be kept in mind that we are dealing here with raw materials or wastes, which likely differ in chemical composition (concentrations, mineralogy, granulometry and presence of contaminants) and therefore might also differ in their hazardous potential.

According to the performed hazard assessment, only 23 of the 168 commodities were identified as potentially HME according to the MARPOL criteria. According to our assessment, the majority of schedules listed in the IMSBC Code are identified as not to be classified HME. These include all agricultural and forestry goods and coal, but

also many salts, most mineral ores, and some refined metals. None of the major bulk commodities iron ore, coal, grain, bauxite/alumina or phosphate rock was identified as HME.

5. Emissions to the marine environment

Two different entry routes are identified which comprise accidental releases (ship casualties, ship losses) and operational releases (dumping or discharging of cargo residues after fine cleaning or washing of cargo holds after unloading) (Reid and Meadows, 1999).

5.1. Accidental release

Oil or chemical tanker casualties typically attract high media coverage. Although bulk carrier losses are more frequent, they usually do so without notice by press and public (Grundy, 2003). Based on different reports (Roberts and Marlow, 2002; Stopford, 1998), data by the International Association of Dry Cargo Shipowners cited by Grundy (2003) and data gathered and kindly provided by Germanischer Lloyd, we identified 503 bulk cargo vessels lost between 1978 and 2012. For 239 of these vessels, no information on the cargo identity was available. For the rest a bulk cargo name was assigned. Based on this information, 23 casualties involved cargoes identified by our assessment as potentially HME (Table 2).

The exact amount of cargoes involved was not reported. Therefore, in this analysis we used the dead weight tonnage (DWT), the maximum weight (load) in tonnes a vessel can carry, which is not a permanent part of the structure of the ship, e.g. cargo, stores, fuel, and crew. As an estimate of the total cargo carried in bulkers we applied a typical converting factor of 0.91 from DWT to tonnes of dry bulk cargo (Endresen et al., 2004). In total, since 1978, approximately 658,000 tonnes of potentially hazardous cargoes was lost at sea, which represents roughly 20,000 tonnes per year. Copper and nickel ores and concentrates accounted for the major part (300,000 tonnes each). When extrapolating these data, in average, almost 10,000 tonnes of copper and nickel ore might enter the marine environment annually as a consequence of ship casualties. It has to be kept in mind that cargo information was available for about 50% of sunken ships, only. Real inputs are likely to be higher assuming that HME classified cargoes were also transported in those ships for which we could not locate information on their cargoes.

5.2. Cargo residue discharge

Dry bulk cargoes carried on bulkers can enter the marine environment at different phases during transport: loading, transhipment, unloading and washing of cargo holds. We tried to estimate the amounts of cargo losses in two ways:

- (i) People involved in cargo handling operations report about cargo residues remaining on hold and deck surfaces and in structural elements of the ship. Experts assume that about 0.05% of the cargo is lost (e.g. unloading with grabber, washing cargo contaminated surfaces and holds), although this value may depend on the physical properties and on the commercial value of the good. Based on the total bulk quantities shipped of estimated 4.3 billion tonnes, it is likely that at least 2.15 million tonnes per year are discharged into the oceans, mainly the coastal sea.
- (ii) Shippers provided oral information during the IMO meetings that 60–100 tonnes of cargo slurry are typically discharged after washing per hold. An average bulker has 5 cargo holds (4 to 7 holds per vessel are common). In 2013, 10,800 bulk cargo vessels were operating worldwide. Assuming that the slurry contains 5% of solids in washing water and 20 washing operations per year and per vessel are likely to be carried out, we estimate that 3.2 million tonnes of solid bulks are discharged per year

Table 2

Overview on sunken bulkers carrying HME cargo.

Cargo		Name of vessel	Dry weight tonnage (DWT) Estimated cargo volumes ^a		Total cargo volume	
			[tonnes]	[toffnes]	[tonnes]	
Mineral concentrates (copper ore/copper concentrate)	1981	GOLDEN PINE	20,349	18,518)	
Mineral concentrates (copper ore/copper concentrate)	1982	DEKA CONCORDE	23,969	21,812		
Mineral concentrates (copper ore/copper concentrate)	1982	MAUREEN B	19,776	17,996		
Mineral concentrates (copper ore/copper concentrate)	1987	QUATSINO SOUND	29,819	27,135		
Mineral concentrates (copper ore/copper concentrate)	1987	PAC BARONESS	26,681	24,280	202.002	
Mineral concentrates (copper ore/copper concentrate)		SINGA SEA	26,486	24,102		
Mineral concentrates (copper ore/copper concentrate)	1990	PEONYL ISL S	26,400	24,024	Cu containing ores	
Mineral concentrates (copper ore/copper concentrate)	1991	POLLUX	13,451	12,240		
Mineral concentrates (copper ore/copper concentrate)	1998	INCE EXPRESS	45,877	41,748		
Mineral concentrates (copper ore/copper concentrate)	2000	CHINA PROGRESS	45,090	41,032		
Copper-/zinc concentrate	2005	AURELIA	34,170	31,095	J	
Mineral concentrates (galena)	1984	PONTESCO	9261	8428	54 501	
Mineral concentrates (lead)	1987	DAYSPRING	21,241	19,329	(J4, J01 (Ph containing oros	
Mineral concentrates (zinc/lead)	1980	CAPIRONA	29,389	26,744) PD containing ores	
Mineral concentrates (nickel ore)	1988	MEGA TAURUS	30,413	27,676)	
Mineral concentrates (nickel ore)	1990	ORIENTAL ANGEL	21,373	19,449		
Mineral concentrates (nickel ore)	1998	SEA PROSPECT	21,297	19,380		
Mineral concentrates (nickel ore)	2010	NASCO DIAMOND	56,893	51,773	286,378	
Mineral concentrates (nickel ore)	2010	JIANFU STAR	44,080	40,113	Ni containing ores	
Mineral concentrates (nickel ore)	2010	HONG WEI	50,149	45,636		
Mineral concentrates (nickel ore)	2011	VINALINES QUEEN	56,040	50,996		
Mineral concentrates (nickel ore)	2011	JIN MAO 9	34,456	31,355	J	
Zinc ashes UN 1435	2000	THOR EMILIE	2130	1938	1938	
Total					657,894	

^a Total cargo volumes carried were estimated by application of a converting factor of 0.91 between tonnes of dry bulk cargo and dead weight tonnage (DWT).

(10,800 bulkers * 5 holds * 20 washings * 60 tonnes slurry * 5% solids).

It has to be understood that these calculations are based on estimations as outlined and informal non-validated information on different aspects of unloading from interviewing a number of experts from the trade. However, both estimations are reasonably close and may indicate the order of magnitude of potential inputs. According to these considerations, we estimate a total annual input of bulk cargoes into the marine environment of more than 2.15 million tonnes. Most are, however, bulks which are unlikely to induce adverse effects to the marine environment or human health, i.e. all major bulks (coal, iron ore, grain etc.) have a low hazardous potential. The quantities of HME classified cargoes discharged are more difficult to estimate as little information is available on shipped volumes. We therefore looked at the world metal production volumes. As ore mines and metallurgic production sites are often at distinct locations, the majority of ores will be shipped. As a rough estimation, we assume that all metals are shipped at least once in form of a typical ore or mineral concentrate. According to the metal content in typical ore concentrates (i.e. most common copper mineral is Chalcopyrite CuFeS₂; an average copper concentrate contains 26% of copper (European Copper Institute, 2014)) we estimated the total amount of shipped ores resp. concentrates (Table 3).

In total, estimated volumes of shipped ores and concentrates of the five metals mentioned in Table 3 sum up to 157 million tonnes, which

would represent 4% of total bulk quantities (4.3 billion tonnes) shipped (UNCTAD, 2014). The shipped and subsequently discharged quantities of different minerals vary according to the production volumes and the concentration of the regarded metal in a typical concentrate. Based on the considerations detailed above, we assume that a minimum of 0.05% is lost during shipping, resulting in annual inputs of 78,500 tonnes of HME ores. This amount largely exceeds inputs from ship casualties, which were estimated at 20,000 tonnes per year. For accidental and operational inputs combined, we estimate inputs of approximately 100,000 tonnes of HME cargoes into the marine environment. These figures are, however, rough estimates. Many ores and concentrates contain different metals (e.g. nickel-copper concentrate), which were not regarded separately. Therefore the total annual amount of metals discharged in the marine environment could be even higher.

6. Effect assessment of bulk cargo discharges

For any kind of risk assessment, information on hazard and exposure (or at a minimum emission data as a surrogate) is needed. Due to the outlined difficulties in assessing the hazardous properties of bulk cargoes and the uncertainties concerning exposure a comprehensive environmental risk assessment is not realistic at present. The estimated annual operational inputs of 2.15–3.2 million tonnes of solid bulk (including 78,500 tonnes of HME bulk) entering the marine environment are considerably larger than oil inputs into the marine environment

Та	ble	3
14	DIC	-

Annual metal production and estimated shipped ore volumes.

	11				
	World annual production from mining [10 ⁶ t] ^a	Typical mineral	Average metal content of ore/concentrate shipped	Estimated shipped ore/concentrate quantity [10 ³ t]	Estimated dumped ore/concentrate quantity [10 ³ t]
Copper	17.9	CuFeS2 ^b Cu5FeS4, Cu2S, CuS	26% ^b	66,000	33
Lead	5.4	PbS, PbCO ₃ , PbSO ₄	50-70	9000	4.5
Manganese	17	MnCO ₃ , Mn ₇ SiO ₁₂ , MnO ₂	35-54% ^a	38,000	19
Nickel	2.5	(Fe,Ni) ₉ S ₈ ^c	10–20% ^c	17,000	8.5
Zinc	13.5	ZnS	50%	27,000	13.5
Total				157,000	78.5

^a Based on U.S. Geological Survey (2014).

^b European Copper Institute (2014).

^c British Geological Survey (2008).

released from ships estimated to represent 457,000 tonnes (GESAMP, 2007). These inputs are not equally distributed. Dumped cargo residues may concentrate within specific sea areas along main shipping routes after leaving unloading ports with discharges only permitted outside the 12 nautical miles zone off shore. Casualties will induce a localised accumulation of potentially toxic material.

One approach to the assessment of effects of bulk cargoes to the marine environment would be the evaluation of accidents. From information collected for more than 500 vessels lost during the last decades, we identified those few cases where effects on the receiving marine environment were studied. Unfortunately, for those 23 bulkers that carried cargoes identified in our study as potentially hazardous to the marine environment "HME" (Table 2), we could not identify any report on the affected marine environment when searching scientific and maritime journals and the internet. Some reports on casualties of bulker carrying non-HME cargoes however exist:

In 1975, the general cargo ship M.V. Lindenbank drifted onto the reef at Fanning Island in the central Pacific and dumped 17,797 tonnes of cargo (mainly vegetable oil and copra) onto a pristine coral reef (Russel and Carlson, 1978). Although no toxic substances were dumped, fish, crustaceans and molluscs died probably due to asphyxiation and clogging of the digestive tract. A green algal bloom was observed. This example shows that environmental effects can be induced by nontoxic cargo releases into sensitive environments.

In 1996 the vessel *Fenes* ran aground within the Lavezzi Islands' Nature Park, South of Corsica, France. There was no oil pollution. The seagrass bed, including the protected species Posidonia and sessile animals, were covered by a thick layer of wheat, ranging from dozens of centimetres to several metres. Although only about 3000 tonnes of wheat were released, eight hectares of Posidonia had been affected. A complete destruction of the grass beds has been reported on an area of 2500 m² covered by Posidonia. Emissions of hydrogen sulphide as well as significant quantities of methanol and ethanol generated by the wheat degradation processes in the polluted area affected the work of rescue personnel severely (http://www.cedre.fr/en/spill/ fenes/fenes.php). This accident showed that even edible grain (which does not fall under the regulation discussed here) when discharged into a coastal zone could form a layer on the sea bottom releasing toxic gases and destroying marine life.

In 2000, the carrier *Eurobulker IV* carrying 17,000 tonnes of coal sank at the southern coast of Sardinia in the Mediterranean Sea. Mechanical phenomena like smothering of vegetation related to the coal were noted. Chemical analysis of the sea water showed no significant results as the wreck lay in a zone of heavy industrial metal contamination. Specific studies on accidental coal immersion (Cabon et al., 2007; Jaffrennou et al., 2007; Lucas and Planner, 2012) showed that most effects were physical and no significant release of noxious inorganic compounds could be measured. The study suggests that the environmental impact of such type of accident would be limited to local smothering effects.

These cases show that cargoes that do not fall under the criteria introduced under MARPOL Annex V for operational discharges may even induce localised effects when released in large quantities. Other effects such as population changes due to eutrophication resulting from large amounts of nutrient inputs in a confined bight, e.g. from a casualty involving a bulker carrying fertilisers in a coastal zone, are plausible. Anyway, the MARPOL Annex V criteria were not intended for specification of risks involved in accidental discharges.

7. Discussion

Our analysis shows that the operational disposal of cargo residues is responsible for inputs of large quantities of solid material into the marine environment. In total, operational inputs of solid bulk cargoes were estimated to exceed 2.15 million tonnes per year, of which 78,500 tonnes was identified as potentially hazardous to the marine environment. The sheer mass of inputs indicates that there is a problem that needs addressing. However, currently available information is not sufficient for any definite statement on the risk for the marine environment generated. The member states of IMO approached this challenge by prohibiting dumping of the most hazardous cargoes.

However, the IMSBC Code, which is the IMO reference for safety requirements for the transport of solid bulk cargoes was not intended for and does not provide information on potential hazards to the marine environment of cargoes listed. Therefore, in 2012 the Marine Environment Protection Committee of IMO agreed on criteria for assignment of cargoes as Hazard to the Marine Environment based on hazard classes with reference to the GHS. In 2016, it was decided that the classification criteria and the shipper's declaration of solid bulk cargoes as to whether or not they were harmful to the marine environment should be made mandatory in the future (IMO, 2016 cf. § 13.14–15).

The criteria seem reasonable as they approach environmental challenges such as ecotoxicity (criteria 1 and 2), littering (criterion 7), and human health hazards via seafood consumption (criteria 3–6). They are similar to those criteria used for liquid bulk cargoes regulated under MARPOL Annex II. However, the direct application of these GHS criteria as hazard indicators appears not well adapted to dry bulk cargoes as they were mainly developed for well-defined organic chemicals, whereas the majority of bulks, which are potentially HME, are mineral ores and metal concentrates with variable composition and physico-chemical characteristics. We have identified several topics which may lead to ambiguities for classification purposes: notably bioavailability, bioaccumulation and degradation.

7.1. Bioavailability/solubility

In ores, metals are present as sulphides, oxides, sulphates etc., which are typically characterised by a low solubility. However, the classification of hazards to aquatic organisms typically relies on the soluble ionic form of the compound. The GHS (United Nations, 2015) recognises this problem and gives specific guidance on hazard assessment and on transformation/dissolution (TD) of metals and metal compounds in aqueous media (based on OECD guidelines). In this context, transformation is understood as potential oxidation and/or interaction of metal and metal compounds with media components. The TD protocol can be conducted for fresh water and marine conditions media with specific ion composition and pH ranges. Environmental classification can then be performed by comparing the environmental soluble metal ions, measured after TD, with their ecotoxicity reference values. It has to be pointed out, that, implicitly, the fraction of metal, which is non-soluble within the contact time of 7 or 28 days, is considered being not hazardous. However, this is not strictly speaking true, as metal particles will continue to release ions and form non-metallic species (ions, salts) over time. Anyway, a similar approach is followed in Europe for the classification of waste where classification is based on the results of biotests performed on eluates of solid wastes (Pandard and Römbke, 2013).

Experience shows that there is very little test data available for even common metal salts using the TD protocol. Even less data exist for metal ores. A study on metal releases of 12 natural copper ores and 8 pure copper minerals showed that depending on the specific composition between 1 and 20% of copper contained in the mineral can be released to freshwater media using a standard TD protocol in 28 days (European Copper Institute, 2014). For some other metals, which can be present in copper ores such as lead (present up to 12.5%), soluble contents between 11 and 53% have been reported (European Copper Institute, 2014). It is this fraction of the total metal content that is used for the hazard assessment for aquatic life according to the GHS. However, it is not clear how weathering in ocean water (e.g. marine salinity and redox potential) impacts the bioavailability of the different metal ores. Schaider et al. (2007) described that physical and chemical weathering can shift metal sulphides with low bioavailability into relatively labile and bioaccessible forms. More generally, it has been reported that relatively insoluble sulphides can be transformed to more soluble sulphates in oxidising marine conditions. Furthermore, insoluble oxides can suffer reductive dissolution which will also liberate associated trace elements (Dold, 2014). As information on composition and bioavailability is missing, in this study, we based our assessment on the assumption of high bioavailability of metal ions as a worst case approach.

7.2. Bioaccumulation

As noted above, the GHS classification of hazards to aquatic organisms relies on the soluble form of the compound. However, for the classification of health hazards (such as CMR and STOT), the GHS considers solubility, bioavailability or degradation potential as irrelevant. This is due to the fact that the GHS aims to classify according to the intrinsic health hazards of a chemical and does not aim at risk assessment under specific exposure conditions. However, under the MARPOL Annex V approach for classifying an environmental hazard, CMR (and STOT) compounds are only classified as HME if they are "having high bioaccumulation" and are "not rapidly degradable". This approach combines GHS criteria of "health hazards" and "hazards to aquatic organisms", which are not commonly assessed in combination. Such approach is related to the PBT concept introduced in the Stockholm Convention (UNEP, 2009), which considers compounds being of special concern if they are not degradable (persistent), bioaccumulative and toxic. Although considering the same phenomenon, the applied thresholds differ, i.e. a bioconcentration factor (BCF) ≥ 500 triggers an assignment for a bioaccumulation potential in the GHS vs. BCF > 2000 and >5000 are used for the identification of *bioaccumulative* and *very* bioaccumulative substances respectively in the Stockholm Convention. Although the term "having high bioaccumulation" used in the MARPOL Annex V differs from the terms used in the GHS and the Stockholm Convention, it is not further defined. Anyway, typically for metals BCFs are regarded as not very meaningful as they are not linked to any intrinsic compound property. Unlike for lipophilic organics, which are taken up via passive diffusion, active transport mechanisms are involved in the metal uptake. Bioaccumulation of metals is much more complicated than for organics for which these criteria were developed and depends on the speciation (i.e. interaction with milieu chemistry), the role of the mineral for the organisms (essential/non-essential), and species-specific effects (i.e. uptake and excretion rates etc.) (Luoma and Rainbow, 2005). Furthermore, it is typically inversely related to exposure concentrations and can vary over several orders of magnitude (Cardwell et al., 2013; Tanaka et al., 2010). BCFs above 500 were reported for $Cd < 0.14 \mu g/L$, $Cu < 2 \mu g/L$, $Zn < 90 \mu g/L$ and a BCF of approx. 500 for $Pb < 2.4 \mu g/L$ (Tanaka et al., 2010). However, these values describe bioconcentration, i.e. the direct accumulation in aquatic organisms from the water. In the marine environment, higher trophic-level consumers may also be exposed to contaminants via the food chain or by ingestion of particles potentially resulting in biomagnification.

7.3. Degradation

For classification as HME according to MARPOL criteria, CMR and STOT compounds have to be "not rapidly degradable". Initially, the problem of non-degradability and persistence was recognized and introduced into regulation for organic chemicals such as PCBs, DDT etc., which may persist for long periods of time, be transported by drift or along the food chain to remote areas and induce toxic effects. However, for inorganic compounds such as metals and metal compounds, which represent the vast majority of bulk cargoes, "the concept of degradability ... has little to no meaning" (United Nations, 2015 § 4.1.2.12.1). Mineral compounds are not degradable. Solubilised minerals may interact with the media and produce insoluble complexes, which might precipitate. Some experts consider complexation as some kind of pseudo-degradation (commonly named "rapid removal"-approach) as being

equivalent to "rapid degradation". In the regulatory context in the EU, the application of this approach for hazard classification purposes was recently rejected by the Committee for Risk Assessment (RAC) (ECHA, 2014) as for a valid estimation of removal, detailed information on media chemistry and reaction constants would be required. These RAC arguments should be particularly important for the marine environment.

In this context it is interesting to note that a contrary approach is followed by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) for hazard rating. GESAMP experts consider inorganic substances that are (readily) dissolvable/ dispersible in water as being equivalent to compounds, which are "readily biodegradable" (GESAMP, 2014). The rationale behind this approach is that the aquatic toxicity of these dissolved compounds can be assessed in the same way as for soluble organic compounds, which are mainly addressed by GESAMP. However, this does not imply that compounds are potentially regarded as less hazardous if they are transferred to a soluble form. Typically the soluble form has the highest bioavailability and is most toxic (Burton, 2010). The hazard rating by GESAMP is only used for classifying bulk liquids under MARPOL Annex II. Under this regulation, liquid cargoes rated "not readily dissolvable/dispersible" would be treated like not readily biodegradable substances falling under strict discharge restrictions. Cargoes rated as "inorg. readily biodegradable" would be classified according to their acute or chronic aquatic toxicity. When transferring this concept in analogy to the classification of dry cargoes, it would result in strict discharge restrictions for substances falling under the "rapid removal" approach.

More sophisticated approaches may be needed in order to address fate and biological effects of metals released into the marine environment.

7.4. Regulative issues

Our analysis shows that criteria proposed by IMO to classify cargoes as HME, and thus to restrict discharge according to MARPOL Annex V, are not well adapted to the materials typically transported as solid bulk. There is ambiguity in the scientific evaluation of bioavailability, bioaccumulation and degradation of mineral which results in conflicting classifications. The current regulation asks the shippers to classify whether or not a specific cargo falls under the HME criteria. However, this classification suffers not only from the ambiguities just explained but additionally from the lack of available information concerning chemical composition, bioavailability, and bioaccumulation of specific components of the cargoes shipped. Industry has started to provide some information on copper ores (European Copper Institute, 2014), but similar information for other shipped goods is still needed. No rules exist about the testing procedures to be used, e.g. transformation/dissolution tests using marine waters.

It could be questioned whether MARPOL Annex V for garbage is the best regulation to tackle cargo residue discharges. The responsibility of declaration relies on the shipper, commonly a company operating a mine on the mainland, and this regulation either allows or restricts disposal. A specific regulation for cargo residues similar to the regulation under MARPOL Annex II for liquid bulk cargoes could be more appropriate as the very specific characteristics of handling could be better addressed (e.g. definition of specific discharge requirements or maximum volumes of discharge according to cargoes specification). The evaluation of liquid bulks is performed by a dedicated expert group of GESAMP operating since the 1970s in order to establish a globally accepted list of hazard assessments of cargoes. There is a need for more precise information on the composition of the commodities, especially relative to components and added chemicals that might prove environmentally harmful. This could then be used for definition of cargo specific rules for hold cleaning and residue discharge. A similar approach has been agreed on in the Convention on the Collection, Deposit and Reception of Waste Generated During Navigation on the Rhine

and Other Inland Waterways (CDNI, 2014) in Europe, which defines conditions whether holds can be washed as such or have to be pre-cleaned (swept or vacuum cleaned) and whether wash water can be discharged into the river, the sewage or needs special treatment.

Furthermore, currently little is known about the identity and the amounts of cleaning agents used for dry bulks. The MARPOL Annex V guidelines (§ 1.7.5 in IMO, 2012a) established non-mandatory hazard criteria for cleaning additives, similar to the HME criteria for the cargoes. These criteria differ strongly from those used for cleaning additives for chemical tankers under MARPOL Annex II. Unlike for the latter, no authorisation processes for cleaning agents used in dry bulk holds are established on the IMO level. However, the influence of these cleaning agents needs to be analysed as these products may influence the solubility and thus the bioavailability of certain metals, in particular when containing chemically complexing agents. As solubility and bioavailability are key parameters for the assessment of the potential risks induced by bulk cargo discharge, a comprehensive assessment should account for the real discharge, i.e. the mixture of cargo slurry and cleaning additive. Under a specific regulation, an international expert group could evaluate the specific hazards created by such discharge procedures.

7.5. Non-hazardous products?

Our analysis was conducted for screening purpose and to evaluate a new regulation designed to protect the marine environment. However, our analysis does not allow conclusion whether bulk cargoes identified as potentially hazardous according to the MARPOL Annex V criteria actually present an environmental or health risk, or whether risks from bulk cargoes not identified as HME can be excluded, e.g. cargoes assigned to IMSBC schedules for radioactive material are not covered by these criteria making the discharge of radioactive ores legal under these guidelines. As shown for coal, representing one of the major bulks, toxic effects of leachates and physical effects of these non-HME classified cargoes have been observed (Ahrens and Morrisey, 2005). Furthermore, leaching of PAHs from coal have been reported (Ahrens and Morrisey, 2005), which are bioaccumulative carcinogens and photosensitizers. Dumping of coal residues is not restricted by the current MARPOL Annex V criteria. The HME criteria are intended to regulate operational discharge only. Accidental discharge of large quantities of non-HME classified cargoes will likely produce a localised effect. A large volume of a fertilizer cargo (e.g. 80,000 tonnes of a typical bulker size) might significantly damage marine life by oxygen depletion (hypoxia) in enclosed sea areas.

8. Conclusion

We would like this paper to sensitise marine scientists to the potential threats for the marine environment (including human health) created by dry bulk shipping. Our analysis should provide a starting point for further investigations. The sheer mass of inputs estimated to exceed 2.15 million tonnes per year should be seen as an obligation for a better quantification of inputs, exposures and hazards of materials involved in order to allow a more conclusive risk assessment. Currently available information is not sufficient for a definite statement on risks for the marine environment generated by dumping of dry bulk cargoes. Bulk cargo names identified as including potentially HME classified cargoes are in general referring to compounds, which are well known as challenges for marine environment protection policy. These bulk cargoes are either composed of metals known for their environmental impact or include shredded plastic materials that will in the long run contaminate the oceans as microplastic (GESAMP, 2015).

There are scientifically critical issues in assessing the bioavailability of metals from ores and concentrates in the marine environment. The questions surrounding classification according to criteria rapid degradation, bioaccumulation, and the implementation of the transformation/ dissolution protocol and its interpretation through clear criteria need regulatory guidance. The aquatic and human health criteria form a potentially solid hazard basis but MARPOL Annex V seems not to be the appropriate instrument to keep these kinds of pollutants out of the sea.

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