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Review

Review on hazardous and noxious substances (HNS) involved in marine spill incidents—An online database

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HIGHLIGHTS

- Online database of hazardous and noxious substances involved in spill incidents.
- Focus on the fate and weathering of HNS involved in previous spill incidents.
- Information systematized for stakeholders involved in preparedness and response.
- Analysis of 184 spilt HNS in 119 incidents in marine waters around the world.
- Very little information on fate and weathering recovered due to poor documentation.

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ABSTRACT

In this review, we have collected information on the behavior, fate, weathering, and impact of hazardous and noxious substances (HNS) accidentally spilled at sea on the marine biota. The information was compiled on a datasheet and converted into a database that can be accessed by the general public (www.ciimar.up.pt/hns). Systematization of data is important to assist stakeholders involved in HNS spill preparedness and response, facilitating the incorporation of lessons from past incidents in the decision process. The database contains 184 entries of HNS spilled in 119 incidents in marine waters around the world. Data were analyzed in terms of HNS physical behavior in water according to SEBC (Standard European Behavior Classification) codes. The most common products involved in accidental spills in the marine environment were identified and major lessons highlighted. From the analysis, it was determined that most HNS spills were poorly documented and information was mistreated. In most cases, no monitoring programs were implemented following the incident. This conduct has occurred in 24 out of 119 incidents analyzed and has consequently limited the information on fate, behavior, and weathering of HNS spilled that could have been recovered. Major gaps were identified, and priorities and recommendations were drawn as a step toward improving preparedness and response to HNS spills.

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1. Introduction

Hazardous and noxious substances (HNS) are defined as any substance other than oil, which if introduced into the marine environment, are likely to create hazards to human health, harm living resources and other marine life, damage amenities, and/or interfere with other legitimate uses of the sea [8]. Transport by sea provides the lower cost solution for the carriage of large quantities over long distances [6]. HNS transported by sea represent 11% of the chemicals traded worldwide [18]. Its volume has multiplied by 3.5 in the past 20 years, and a 16% increase is forecasted by 2015 [18], increasing the risk of accidental spillage. Moreover, increased trade among major ports generates highly frequented zones, often in narrow straits and channels, where the risk of spillage is further increased [1,2].

The severity of a spill impact depends on several environmental variables, such as, the location of the spill, weather conditions, properties of the hazardous substances transported, and ways such substances are packaged and stowed. HNS spills are different from oil spills, given the wide variety of products that may be involved, either separately or as mixtures, with different fate and weathering characteristics. Whereas, most oils initially float on the sea and are immiscible with water, HNS chemicals exhibit a wider range of behaviors (i.e., sinking, floating, gassing/evaporating, and dissolving) and toxicities to marine organisms [5]. A considerable amount of information is required for risk assessment and an effective decision-making process in the case of a HNS spill, which has led authorities, environmental managers, and the scientific community to focus on specific preparedness and response solutions. Immediate short-term decisions related to spill containment, recovery and safety, as well as medium and long term decisions related to the environmental impact and impact on human health, need to be well-founded. The similarities and differences between oil and HNS need to be considered in order to assess the suitability of existing arrangements for incidents involving HNS [26].

A particular gap in information exists regarding the short-term behavior of HNS once spilled at sea. The available models, similar to those developed for hydrocarbon spills, usually make use of substance properties obtained in the laboratory that differ from the real conditions at sea [1,2], and they do not take into account the time factor and meteorological conditions, the two critical parameters during a spill incident [19]. Another known gap is related to the acute and chronic toxicity data for marine organisms. These data are scarce, often inferred from fresh water species or predictive models, and very rarely measured under real conditions on adequate bioindicator species. Ecotoxicological data for most priority HNS are not available, neither for single nor mixtures exposure [24]. Databases and factsheets can be very useful in collecting this information and making it available to the community.

The present review aims to compile and assess existing information on HNS marine spills and to build an online database accessible for stakeholders, focused mainly on the fate, behavior, and weathering of HNS at sea, and toxicity to marine organisms. Additionally, we have identified major gaps and drawn priorities and recommendations, as a step toward improving preparedness and response to HNS spills. This work was conducted on the frame of the Atlantic Region Transnational Programme – ARCOPOLplus.

2. Methodology

Information on HNS spill incidents that occurred worldwide in seawater was analyzed. This information was collected from the internet, websites of public and private institutions that address marine contamination, official and unofficial institutional reports, project reports, scientific papers, congressional outputs, and other databases. It was filtered for data on the fate and weathering of the products spilled and for monitoring actions and reports. Only incidents occurring in seawater, where there was an effective partial or total loss of the cargo, were considered. Those incidents where, the cargo was not lost or it was lost in sealed containers and then recovered were not considered. One hundred nineteen HNS spills were compiled in an Excel datasheet (Supplementary material S1). Information concerning each product spilled in a particular incident was inserted in an individual row of the datasheet. A total of 187 entries were created corresponding to 187 substances spilled. For each incident, the information was organized in columns. The header of each column and the description of its content are compiled on Table 1: ship name, incident date, incident location 1, incident location 2, transport mode, amount spilled, HNS spilled, CAS number, chemical formula, physical state, physical behavior, MARPOL category, category according to the IMDG code, subsidiary risk class, classification as marine pollutant, HNS classification, fate and weather facts, and sources of information. The detailed bibliography used for the database, described on the field “sources of information”, is described in detail in the Supplementary material (S2).

Three international codes were used to classify HNS involved in spills and collect information on the behavior, fate, and weathering of the HNS once spilled in seawater: SEBC [28], IMDG [8], and IBC [7] codes. The Standard European Behavior Classification (SEBC) codes provide a set of criteria for the theoretical evaluation of the short-term behavior of chemicals spilled in seawater according to their physicochemical characteristics. Density, solubility, and vapor pressure are the characteristics that most determine short-term behavior of HNS in water. According to these characteristics, HNS are characterized as sinkers, floaters, dissolvers, evaporators, or a combination of two or three of these characteristics.

The International Maritime Dangerous Goods (IMDG) codes define rules for the transportation of dangerous goods by sea, covering such matters as packing, container traffic, and stowage, with particular reference to the segregation of incompatible substances. According to this code, dangerous goods are classified in different classes to define and describe the characteristics and properties of the substances, materials, and articles which would fall within each class or division [8,13]. These characteristics are very helpful in determining the behavior of substances once spilled, including physicochemical characteristics (flammability, oxidizing power, corrosiveness) and toxicity. The code also identifies a number of dangerous substances in the various classes that have been additionally identified as harmful substances to the marine environment (marine pollutants – MP – column O, S1). This classification is in accordance with the criteria for the selection of marine pollutants for the purposes of Annex III of the International Convention for the Prevention of Pollution from Ships (MARPOL), 1973, as modified by the protocol of 1978 relating thereto [21].

The International Bulk Chemical (IBC) codes describe the construction and equipment of ships carrying the dangerous chemicals

Table 1
Description of the fields on supplementary material database (S1) regarding documented HNS spills.

Column	Header	Description
A	Ship name	
B	Incident date	
C	Incident location 1	Country
D	Incident location 2	Europe (E) or rest of the world (RW)
E	Transport mode	Bulk or packaged
F	Amount spilled	Unit is tone (t)
G	HNS spilled	Chemical name of the substance spilled
H	CAS number	CAS number of the HNS spilled
I	Chemical formula	Chemical formula of the HNS spilled
J	Physical state	Physical state of the HNS spilled: gas/solid/liquid
K	Physical behavior	According to SEBC Code. SEBC – Standard European Behavior Classification system (SEBC) [28] – provides a set of criteria for evaluating the short-term behavior of chemicals spilled at sea. Five primary behavioral categories are identified as Gas (G), Evaporators (E), Floaters (F), Dissolvers (D) and Sinkers (S), with combinations being represented as GD, ED, FED, etc. Fp – vegetable oil are classified as floater persistent, as their viscosity is >10 cSt (centistoke; 1 cSt = 1 $mm^2\ s^{-1} = 10^{-6}\ m^2\ s^{-1}$).
L	MARPOL[a] category	HNS are classified according to the new IBC MARPOL (international code for the construction and equipment of ships carrying dangerous chemicals in bulk) categories that entered into force on the 1st of January 2007. Considering bulk liquids, four pollutant categories were established: Category X: compounds deemed to present a major hazard to either marine resources or human health; Category Y: compounds deemed to present a hazard to either marine resources or human health or cause harm to amenities or other legitimate uses of the sea; Category Z: compounds deemed to present a minor hazard to either marine resources or human health; and Other Substances (OS): substances which have been evaluated and found to fall outside category X, Y, or Z because they are considered to present no harm to marine resources, human health, amenities, or other legitimate uses of the sea when discharged into the sea from the tank cleaning of deballasting operations.
M	Category according to the IMDG code	International maritime dangerous goods code IMO, 1965, that became mandatory for adoption by SOLAS-international convention for the safety of life at sea signatory states from 1st January 2004 (IMO) [15].
N	Subsidiary risk class	Contains the class number(s) of any subsidiary risk(s) according to IMDG code.
O	Classification as marine pollutant	Includes substances that are identified as marine pollutant (MP) at the dangerous goods List, of the IMDG code index (Annex III) IMO, 1965 or that meet the criteria for classification as an "Environmentally Hazardous Substance (aquatic environment)" in 2.9.3.3. Section (IMO) [13].
P	HNS classification	Classification according to 2010 HNS convention bulk Oils, carried in bulk, as defined in regulation 1 of Annex I to MARPOL 73/78 Noxious liquid substances, carried in bulk, as defined in regulation 1.10 of Annex II MARPOL 73/78, and those substances provisionally categorized as pollution category X, Y, or Z and listed in MEPC 2 circulars for substances subject to tripartite agreements (IMO) [14] iii. Dangerous liquid substances carried in bulk listed in chapter 17 of the IBC Code (IMO) [11]. v. Liquefied gases as listed in chapter 19 of the IGC Code (IMO) [10]. vi. Liquid substances carried in bulk with a flash point not exceeding 60 °C. vii. Solid bulk materials possessing chemical hazards covered by the IMSBC Code (IMO) [12]. Packaged iv. Dangerous, hazardous and harmful substances, materials and articles in packaged form covered by the IMDG Code, in effect in 1996.
Q	Fate and weather facts	Facts observed and reported relative to the fate and weather of the chemical spilled.
R	Sources of information	Describes the sources where information was collected, including databases, official reports, ad hoc reports and scientific literatures. It is presented at the end of the report.

[a] MARPOL – International Convention for the Prevention of Pollution from Ships – There is no correspondence between new IBC categories with the old categories. The categorization has been revised by the joint group of experts on the scientific aspects of marine pollution (GESAMP) for the purpose of drafting the new IBC code (international code for the construction and equipment of ships carrying dangerous chemicals in bulk) (IMO) [9]. The MARPOL Annex II updated of 1st January 2007 classifies vegetable oils and animal oils (lard and fish oils) as HNS, MARPOL ANNEX II Category Y, i.e., HNS.

in bulk. It provides an international standard for the safe carriage by sea of dangerous and noxious liquid chemicals in bulk. In October 2004, IMO adopted revised MARPOL 73/78 Annex II regulations (1978) for the control of pollution by noxious liquid substances in bulk. Regulations incorporated a four-category categorization system for noxious and liquid substances, according to toxicity, that entered into force on 1st January 2007.

The information collected was inserted into a MySQL (v.5) database. It is possible to use queries to search by ship name, name of the compound spilled, year when the spill occurred, or country where it occurred. The database is hosted at CIIMAR's (Interdisciplinary Center of Marine and Environmental Research) servers and is available worldwide on our website (http://www.ciimar.up.pt/hns) programmed in HTML with PHP scripting.

3. Results

3.1. General results

The 119 spill incidents compiled occurred from 1947 to 2011 and involved 187 spilled substances. Of the incidents reported, 96.7% occurred from 1970 onwards. It was possible to compute 847,774 tons of substances spilled at sea, which is an underestimation of the total, because for 47 occurrences (32%), the amount spilled is unknown. Seventy five of the analyzed incidents (63%) occurred in European waters and 45 in other regions (37%).

Most occurrences involved substances transported in bulk (60%), while 40% corresponded to packaged goods. Twenty one percent of the incidents resulted in mixtures of compounds due to the spillage of more than one chemical.

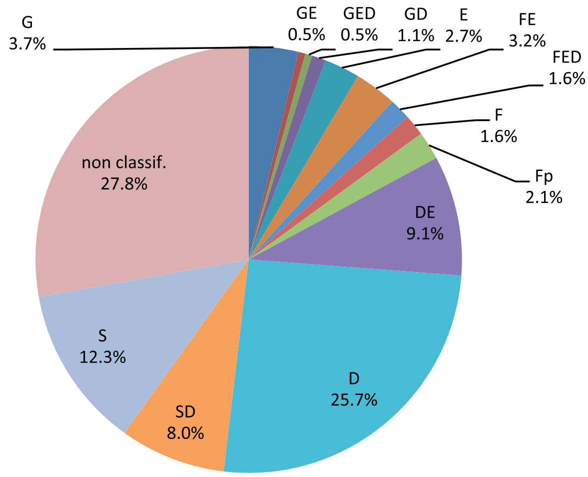

Fig. 1. Classification of the 187 substances involved in the 119 spill events according to the physical behavior described by the SEBC (Standard European Behaviour Classification) code: G–gas, GE–gas evaporator, GED–Gas evaporator dissolver, GD–gas dissolver, E–evaporator, FE–floater evaporator, FED–floater evaporator dissolver, F–floater, Fp–floater persistent, DE–dissolver evaporator, D–dissolver, SD–sinker dissolver, S–sinker, and non classif.–non-classified substances.

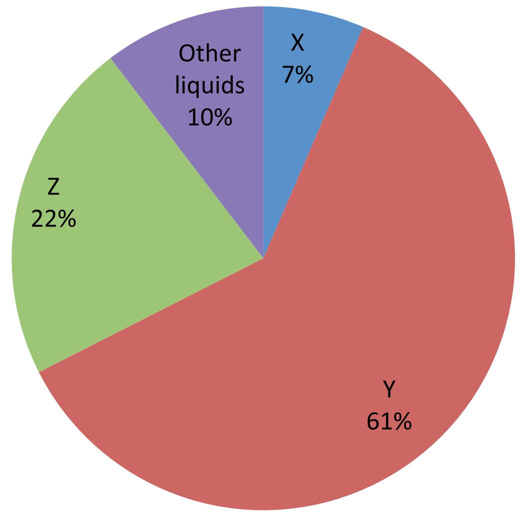

Fig. 3. Classification of the liquids involved in spill incidents according to the new IBC (International Bulk Liquid Chemicals) MARPOL code: X–compounds deemed to present a major hazard to either marine resources or human health; Y–compounds deemed to present a hazard to either marine resources or human health or cause harm to amenities or other legitimate uses of the sea; Z–compounds deemed to present a minor hazard to either marine resources or human health; and OS–other substances which have been evaluated and found to fall outside category X, Y, or Z because they are considered to present no harm.

Considering the physical state of the goods involved in the incidents, 44% were liquids, 42% solids, and 8% were gases. Ten percent corresponded to incidents where the spilled goods were a mixture of many non-classified substances or the information provided was not enough to classify them.

Regarding physical behavior (Fig. 1), the goods most involved in spills were dissolvers (25.7%), followed by sinkers (12.3%), dissolver evaporators (9.1%), and sinker dissolvers (8%). All of the other behavior classes were represented below 5%. Twenty eight percent of the substances are not classified.

According to IMDG code classification, 21% of the spilled substances belonged to class 3 (flammable liquids), 16% to class 6.1 (toxic substances), 13% to class 5.1 (oxidizing substances), and 12% to class 8 (corrosive substances) (Fig. 2). All of the other represented classes were below 10%. Five percent of the substances are classified as MHB (material hazardous only in bulk) and 10% are not classified because they are not considered dangerous goods.

Twenty one percent (21.2%) of the substances involved in spills were classified as marine pollutants, mostly belonging to class 6.1, which included various biocides (carbofuran, dieldrin, dinoseb, epichlorohydrin, endosulfan, ethoprophos, lindane, methamidophos, niclosamide, propineb, pentachlorophenate, and pentachlorophenol), lead compounds (tetraethyl lead, tetramethyl lead, and organic lead), and cyanide derivatives. Only one compound was classified as class 9, miscellaneous dangerous substances and articles – the pesticide niclosamide. This class contains marine pollutants that present a danger not covered by other classes.

From the liquid substances reported, 7% were classified as belonging to X category (compounds deemed to present a major hazard to either marine resources or human health) according to the new IBC Code (MARPOL Annex II), 61% as Y category (deemed to present a hazard), 22% as Z category (deemed to present a minor hazard), and 10% as other substances (OS) (Fig. 3). The most common products involved in marine accidental spills were classified in eight groups according to their use (Fig. 4). The larger group is that of "chemical products" made in large quantities, the most common being sulfuric acid (6 incidents), calcium hypochlorite (5), and sodium hydroxide (5). Thirty incidents had this group involved. The second larger group is "petrochemical and coal products", which included coal, benzene, dodecylbenzene, alkylbenzene, xylene, toluene, styrene, phenol, hexane, naphtha, and calcium carbide. These compounds were involved in 18 spills. "Pesticides" and "ores and metal concentrates" were each involved

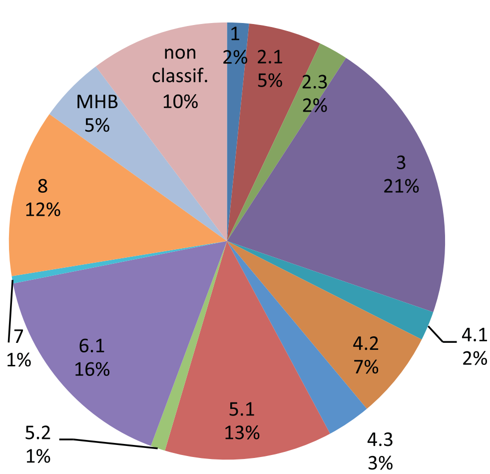

Fig. 2. Classification of the 187 substances involved in the 119 spill events according to the IMDG (International Maritime Dangerous Goods) code. See the description of the classes for the methodology (Table 1).

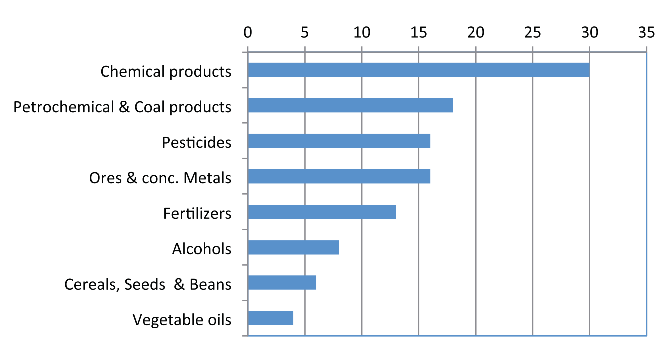

Fig. 4. Categories of the most common products involved in accidental spills in the marine environment according to their use. The *x*-axis corresponds to the number of spills in which the category was involved.

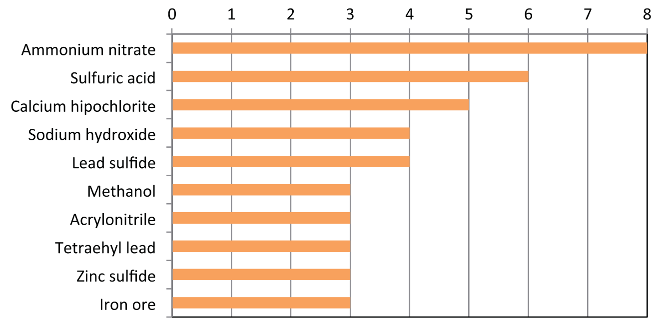

Fig. 5. Most common products involved in accidental spills in marine water. The *x*-axis corresponds to the number of spills in which the substance was involved.

in 16 incidents, followed by fertilizers (13 incidents), alcohols (8), cereals and beans (6), and vegetable oils (4).

Regarding single chemical compounds, the most common was ammonium nitrate (involved in 8 spill incidents), followed by sulfuric acid, calcium hypochlorite, sodium hypochlorite, and lead sulfide (Fig. 5). Twenty three of the incidents compiled involved more than one product.

From the 119 analyzed incidents, it was observed that 54 of them mentioned information regarding the fate and weathering of the spilled substance, and only 24 of the registered occurrences contained some information on environmental or biological monitoring or even any parameter measurements (e.g., pH and product concentration).

We have explored in further detail four categories of HNS that are better documented and cause particular harm to the marine environment: nontoxic dissolvers, nontoxic sinkers, persistent floater vegetable oils (SEBC code), and marine pollutants (IMDG code).

3.2. Spill incidents with nontoxic dissolvers

Most findings seem to indicate that the environmental impacts of nontoxic dissolvers are localized in time and space. In the case of acids and bases, the monitoring of pH showed alterations of the normal seawater values that returned to normality within hours or days, depending on the depth of the water column and hydrodynamics, and in various cases, no environmental harm was reported. However, the effects greatly depend on the local conditions. The recovery of dissolvers (acrylonitrile) has been attempted.

Some plumes of dissolved chemicals may, in theory, be neutralized, oxidized, flocculated, or reduced by the application of other chemicals (http://www.itopf.com/marine-spills/about-hns/). The controlled release of soluble, hypothetically non-toxic and non-bioaccumulative cargo has been considered an acceptable option, depending on environmental sensitivity. Acute effects, such as, the death of fish and birds, have been reported, and, in shallower waters and sensible ecosystems, the direct and indirect reactivation of toxic metals adsorbed in the sediments, causing longer term effects, has to be considered. The dilution or neutralization of the spilled chemical has also been recognized as a possible action to implement under specific circumstances.

In the case of ammonium nitrate, which is a fertilizer and strong oxidizer involved in eight major incidents of non-toxic dissolvers, it has been reported to cause algal blooms and severe oxygen consumption that might asphyxiate aerobic living organisms. Most incidents with this compound resulted in explosions and fire. Given the ecological and risk assessments, the decision to dump ammonium nitrate solutions in the open sea has been considered, preferably in batches (*Junior M*).

3.3. Spill incidents with nontoxic sinkers

Incidents involving nontoxic sinkers (e.g., cereals, seed, beans, and some ores) are reported to cause a mechanical phenomenon of vegetation smothering and sediment covering. Depending on the ecosystem sensitivity, they may be more devastating than initially thought. The degradation of cereals causes the emissions of hydrogen sulfide, methanol, and ethanol. The fermentation process of wheat and release of hydrogen sulfide in past incidents seem to be due to the microbial proliferation of sulfate-reducing bacteria. Wheat degradation processes were monitored in the affected areas, in addition to bacteriological development. It was observed that fermentation caused a local decrease in pH that impacted the local marine communities. The reported effects on biota included the death of *Posidonia* beds (*Fenes, Eurobulker IV*) and destruction of coralline community (*Infinity, Lindenbank*). A phenomenon reported in some incidents has been the green algal bloom caused by macro- and micro-nutrients dissolved in seawater, both from the cargo and ship's hull (metals), that stimulate algal growth.

3.4. Spill incidents with persistent floater vegetable oils

Vegetable oil is classified as a persistent floater according to SEBC codes and as an HNS of the Y category according to MARPOL 73/78 Annex II (1978) because it can cause enormous damage as described below. Currently, vegetable oils tend to be transported in larger quantities mainly due to the biodiesel and soap industries. Computer modeling predictions designed for oil spills did not seem to be suited to manage vegetable oil due to its solid state ([3]; *Allegra*). These non-petroleum drifting oils can mix with floating material and form a floating crust or sink. Slicks may come ashore where they tend to beach at the high water mark. Solid pellets, such as, margarine-like rubbery balls or "chewing gum" balls, may be collected by hand. Concrete-like aggregates of sand may persist on the beaches for over 5 years. Tests revealed that molecules of sunflower oil polymerize with wave action, both in seawater and in the intertidal region, forming relatively intractable products [22,23]. Depending on the physicochemical characteristics and environmental conditions, vegetable oil may alternatively disperse naturally in the water column into small particles of only a few millimeters in diameter. This phenomenon explains the disappearing of 870 ton of oil during the *Allegra* spill in the UK ([3,20,4], S1).

Oil and sand may form impermeable aggregates, under which shoreline species are imprisoned, seriously affecting biodiversity. Fish, crustaceans, and mollusks death has been observed probably due to asphyxiation and clogging of the digestive tract. The mussel internal shell also loses its nacre lining, and the external shell becomes chalky. In addition, vegetable oils are a source of natural lipids to the marine bacteria, flora, and fauna. Palm nut oil produces alkanes, esters, aldehydes, and alcohols, some of which are harmful to marine life [20].

3.5. Marine pollutants

The information was collected on HNS of the marine pollutants (MP) category that were involved in spills, including biocides and lead based organic compounds (S1). These compounds should be transported in sealed containers according to maritime transport codes. In various occurrences, it was attempted to recover MP lost cargo containers, total or partially, although drums may be damaged by savage, fishing gear, and by pressure. Fishing and shellfish harvesting may be banned in some cases where a risk to human health is assessed [31]. On the impossibility of finding and recovering cargo, a security radius may be set around the wreck. For toxic substances with low solubility, the possibility of leaving containers on the seafloor should be considered, when they are not expected

Table 2
Summary of the containment action taken and lessons learned from the incidents analyzed in further detail, regarding nontoxic dissolvers, nontoxic sinkers, persistent floaters, and marine pollutants. HNS classes are according to SEBC (Standard European Behaviour Classification) and Annexes II and III of MARPOL 73/78 Annex II (1978).

HNS Class	Spills analyzed	HNS involved	Containment actions taken	Lessons learned
Nontoxic dissolvers	*Alessandro Primo, Bahamas, Cynthia M, EnaII, Ievoli Sun Junior M, Martina, Pacific Adventurer, Panam Perla, Puerto Rican, Viggo Hinrishsen*	Hydrochloric acid Lye/NaOH acrylonitrile sulfuric acid methyl ethyl ketone isopropanol chromium ammonium nitrate	Recovery, controlled release, controlled dump, dilution, neutralization, oxidation/reduction, and flocculation	• Effects are localized in time and space. • When strong acid or bases are involved, pH shows alterations that return to normality within hours or days acute effects on biota may occur. • Controlled release or dumping may be an acceptable solution depending on environmental sensitivity. • Possible reactivation of toxic metals adsorbed to sediments, causing long term effects. • Dumping of strong oxidizers and fertilizers may cause algal blooms and severe oxygen depletion and asphyxiation of aerobic organisms.
Nontoxic sinkers	*Eurobulker IV, Fenes Infinity, Lindenbank*	Coal, wheat, rice, sugar cane, copra, and cocoa beans	Not mentioned	• Mechanical smothering of vegetation or corals. • Algal blooms may occur due to phosphate and nitrogen release. • Proliferation of sulfate reducing bacteria that cause local pH reduction. • Consequences may be more devastating than initially thought.
Persistent floaters	*Allegra, Lindenbank, Kimya*	Vegetable oil, palm oil, coconut oil, and sunflower oil	Not mentioned	• Oil disperses naturally on water column in particles of only few millimeters. • Formation of solid slicks at sea surface that mix with other floating materials forming a crust. • Release of alkanes, esters, aldehydes, and alcohols, some of which are harmful to marine life. • Fish, crustaceans, and mollusks death, probably due to asphyxiation and clogging of the digestive tract. • Beaching of solid 5–50 cm pellets and "chewing gum" balls. • Formation of solid long lasting (up to 6 years) impermeable aggregates under which shore line species are imprisoned, seriously affecting biodiversity. • Coating properties and impacts similar to those of oil spills, affecting sea life, tourism, and yachting. • Computer models designed for oil spills are not suited for vegetable oils that solidify at sea temperature.
Marine pollutants	*Carla, Cavtat, Dana Optima, Erkowit, Kairo, Ever decent, Perintis, Princess of the Stars, Testbank*	Radioactive materials, lindane, permethrin, cypermethrin, and pentachlorophenol	Recovery, fish and shellfish ban, set of security radius, water analysis, monitoring plan, leaving containers at sea floor, air-lift dredging, flocculation, and active carbon treatment	• It may be acceptable to leave containers of very toxic substances with low solubility at seafloor because they are not expected to cause extensive pollution if they leak from the drums. • Drums of cargo left on sea floor may be damaged by salvage, fishing gear and pressure. • Possible contamination of commercial natural and/or aquaculture stocks. • Heavy economic losses due to fishing and shell fishing ban, destruction of aquaculture stocks and regaining of consumers/markets trust.

to cause any extensive pollution by leaking from the drums. After the *Perintis* incident at the English Channel, containers were left on the sea floor, and a monitoring program was conducted over several years on water, fish and shellfish samples by French and British authorities. No lindane pollution was ever discovered. This is one of the few incidents when an extensive monitoring program was launched (S1).

4. Discussion and conclusions

HNS have a wide range of potential fate and behavior characteristics once released into the marine environment. Selection of the appropriate response to an incident requires detailed knowledge on the physicochemical and toxicological properties of the substance involved. The categorization of transported goods according to these characteristics and toxicity is fundamental for preparedness and response to spill incidents. Information on the short-term behavior of the product spilled in seawater makes it possible to define an action plan (e.g., detection, monitoring, and containment) that is well adapted to the geographical location, particular meteorological conditions, hydrodynamics, and characteristics of the water column and sea bottom compartments [20]. In Table 2, we summarize the spill containment actions taken and the most important lessons regarding HNS fate, behavior, and toxicity to marine organisms learned from the incidents analyzed in detail in the results section.

The analysis of the incidents list (S1) emphasizes the need to deepen our knowledge on several aspects related to preparedness and response to HNS spills: i) HNS behavior at sea and the development of HNS detection, forecasting, and risk analysis tools; ii) HNS hazards to humans and marine organisms; and iii) implementation of knowledge at the operational level to improve crisis management.

i) Even though advances in HNS modeling tools have been achieved [1,2], one of the major gaps identified is the limited knowledge on HNS behaviors at sea; this gap should be approached through experiments in the laboratory and at the pilot level involving priority HNS [24]. This will set the foundations for improving modeling tools for forecasting and for following and supporting the initial stages of response operations. In designing the specific models, at least those for the priority HNS transported at sea, the different behaviors classes (i.e., sinkers, dissolvers, floaters, and gases/evaporators) need to be considered. These models should take into account real conditions at sea (temperature, salinity, and density), weather conditions, and time [1,2,19]. Additional work must be conducted for upgrading detection technologies, forecasting, and risk analysis tools developed for oil spills, including forecast models and high-tech detection and monitoring systems.

ii) Data on the hazards of HNS for humans and marine life are essential for the decision-making process and selection of an appropriate response. The importance of evaluating the physicochemical and toxicological properties of a contaminant for remediating environments affected by chemical incidents has recently been addressed [30]. Most acute and chronic toxicity data available for the biota concern fresh-water instead of marine organisms. Accordingly, it is recommended that values and indexes related to acute and chronic toxicity, such as the lowest observed effect (LOEC), no observed effect concentration (NOEC), bioconcentration, bioaccumulation, and biotransformation indices, are determined under real conditions using appropriate sentinel species, instead of being inferred from other species or estimated from predictive models. Additional data on the ecotoxicity of HNS will allow for better estimations of the risks to the ecosystem and draw monitoring programs for particular HNS of concern. The limited information on the impact of HNS spills documented here is, in many cases, due to inaction, but in many others, it is due to the nature of the compounds involved, hostility of the environment, lack of means, lack of expertise and inexistence of a priori elaborated plans to perform post-spill monitoring studies [27]. Monitoring programs aiming to assess the environmental impacts of spills should be launched as soon as an incident occurs. Baseline data from the area, or similar areas, should exist, to make it possible to determine impacts, and access recovery [17,25]. Because 21% of the spills analyzed involved more than one compound, it is also recommended to evaluate the risk of mixtures of HNS. Hazards of HNS are much better documented for humans than for ecosystems, although the effects of mixtures have also been mistreated. These data are of paramount importance for risk assessment when human presence is needed at the spill scenario.

iii) The aforementioned gaps of knowledge and proposed recommendations must form the basis of the priority actions to improve preparedness and response to HNS spills. The implementation of this knowledge at the operation level will allow upgrading HNS pollutant responses protocols, booming/contention protection plans, development of guidelines for volunteers, maritime professionals and local authorities, waste management protocols, educational material and development of pilot, and training exercises. These actions will foster the transfer of knowledge and tools to local authorities and create a network of expertise and resources integrating the industry and major stakeholders. This will allow communities to manage and recover from a pollution incident and increase community resilience and preparedness before, during, and after a shoreline HNS pollution incident by maximizing resources, tools and existing theoretical, and operational knowledge.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2014.11.005.

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