[Draft] HELCOM Manual II

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Response to accidents at sea involving spills of noxious and hazardous substances

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1 Introduction

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The organization of request and provision of assistance for response to emergency situations as well as the principles, management and command structure for operational co-operation between Contracting Parties of HELCOM are described in Volume I of HELCOM Manual on Co-operation in Response to Marine Pollution. The purpose is to improve the co-operation in response to marine pollution within the Baltic Sea area. This volume II of the HELCOM manual is meant as a help for the Operational Control body, the Response Commander, On-Scene-Commanders and other coordinators conducting multinational operations specifically in response to emergency situations involving spills of hazardous chemicals except oil.

The first priority in any emergency situation is to rescue and protect any persons present at the emergency scene such as the crew and passengers of involved ships, responders, rescuers or people otherwise present at the emergency scene and exposed to immediate danger and address the health and safety of the general public in the vicinity by restriction of access to dangerous areas, evacuation, etc. This manual focuses on response measures to prevent additional leakages and to reduce spills and emissions to the environment.

In cases where a Contracting Party is not able to cope with an incident involving chemicals by the sole use of its own personnel and equipment, the Contracting Party can request combatting assistance from other Contracting Parties starting with those who seem likely also to be affected by the spillage.

The co-operation in combatting spillages of harmful noxious substances in the Baltic Sea area is based on the Helsinki Convention and HELCOM Recommendations on combatting matters, adopted by the Helsinki Commission. In accordance with the Helsinki Convention the Contracting Parties shall maintain ability to respond to spillages of oil and other harmful substances into the sea threatening the marine environment of the Baltic Sea area.

The variety of chemicals transported by the sea is too broad and the possible emergency situations involving spills of such chemicals are too diverse to enable detailed operational guidance for the management of all kinds of risks related to substances individually. Instead the aim of this manual is to define a few typical risk scenarios based on grouping of chemicals demanding similar kinds of strategies for response actions.

The first response action to an emergency situation is generally to collect information on the chemicals and spills and the circumstances on the scene. The information is used to create awareness of the situation including the identification of the main potential hazards or risks. An emergency situation usually involves different kinds of risks. The prioritizing of the risks will determine how to initiate response actions. The response actions aiming at reducing the overall harmful consequences of the emergency situation should be chosen according to the most important immediate risk. Every described risk scenario is based on such a priority setting of the main immediate risks involved. However, each risk scenario also contains references to secondary risks which also have to be taken into consideration during the response operation.

The number of scenarios is limited to only a few to give advice on how to initiate the response operation. The response strategy for each operation may be developed and refined during the operation taking into account secondary risks when the main risks are under control.

The Contracting Parties are advised to use also other sources of guidance on single chemicals in addition to this Manual. Examples of such information are mentioned as references in the scenario tables and in chapter 2.5. Important sources are the Marine Chemical Information Sheets (MAR-CIS) prepared by the European Maritime Safety Agency EMSA and Safety Data Sheets or Material Safety Data Sheets (SMS/MSDS) according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) as agreed by the International Maritime Organisation IMO. Remote information and advice on chemicals involved in maritime incidents can also be provided to national administrations by contacting the MAR-ICE Network. MAR-ICE brings together marine pollution response and chemical experts and provides rapid access to professional product and incident-specific information on chemical products

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Commented [WNO2]: Very kind to mention EMSA's MAR-CIS first, but as they only cover ~ 200 substances, I would cite SDS/MSDS first.

Each risk scenario contains references to chapters with general information to support the development of a feasible response strategy for each emergency situation. These chapters give information on methods for estimation and prediction of the spreading of spilled or emitted chemicals, on general actions and tactics and on equipment and methods for effective and safe response measures.

2 Hazards: Definitions, Identification and Assessment

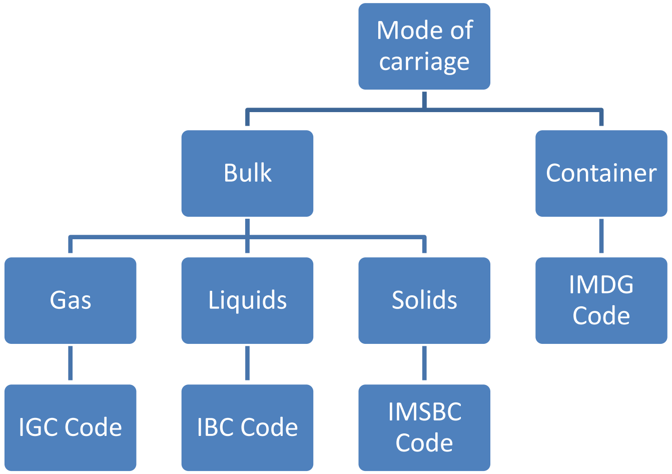
For the purpose of this document, hazardous and noxious substances (HNS) are any substances other than oil which, if introduced into the marine environment are likely to create hazards to human health, to harm living resources and marine life, to damage amenities or to interfere with other legitimate uses of the sea.[1]

To further expand on the definition HNS covers a wide range of items in a variety of forms which may be carried as cargo in both bulk and packaged HNS, therefore it includes dangerous goods (also called Hazardous Materials or HazMat) such as solids, liquids, or gases that can harm people, other living organisms, property, the environment, or the carrier; materials that are flammable, explosive, corrosive, oxidizing, asphyxiating, bio hazardous, toxic, pathogenic, or allergenic. Also included are physical conditions such as compressed gases and liquids or hot materials, including all goods containing such materials or chemicals, or may have other characteristics that render them hazardous in specific circumstances.

Dangerous goods transport must be carried out according to the regulations that are in place to reduce the potential for harm to people, property and environment that may result from a dangerous goods release. The International Maritime Organisation (IMO) has developed various legal instruments related to dangerous and polluting goods differentiating between how the goods are carried (packaged and bulk) and by type of cargo (solid, liquid and liquefied gases). Regulations covering the carriage of dangerous cargoes and the ships that carry these cargoes are found in the International Convention for the Safety of Life at Sea (SOLAS, 1974), as amended, and the International Convention on Maritime Pollution (MARPOL 73/78), as amended. These conventions are supplemented by the following codes:

- International Maritime Dangerous Goods Code (IMDG Code):
- The International Maritime Solid Bulk Cargoes Code (IMSBC Code)
- The International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (IBC Code)
- The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC)

[1] IMO Protocol on Preparedness, Response and Co-operation to Pollution Incidents by Hazardous and Noxious Substances, 2000 (HNS Protocol)


Mode of carriage
Bulk
Container
Gas
Liquids
Solids
IMDG Code
IGC Code
IBC Code
IMSBC Code

2.1.1 IMDG-Code:

- The IMDG contains general requirements for the issuing of detailed standards on packing, marking, labelling, documentation, stowage, quantity limitations, exceptions and notifications. The definition of substances includes mixtures and solutions of substances as well as articles. HNS are grouped into different classes and subclasses of hazards

1	Explosives
2	Gases
3	Flammable Liquids
4	Flammable solids
5	Oxidizing substances and organic peroxides
6	Toxic and infectious substances
7	Radioactive material
8	Corrosive substances
9	Miscellaneous dangerous substances and articles

Marine pollutants are those substances which are identified as in the International Maritime Dangerous Goods Code (IMDG Code) or which meet the criteria in the Appendix of Annex III

- acute aquatic toxicity;
- chronic aquatic toxicity;
- potential for or actual bioaccumulation; and;
- degradation (biotic or abiotic) for organic chemicals;.

The IMDG hazard identification data are: Proper Shipping Name (PNS), UN- Number, hazard class, whether or not a marine pollutant.

2.1.2 IBC-Code:

The IBC gives international standards for the safe transport by sea in bulk of liquid dangerous chemicals, by prescribing the design and construction standards of ships involved in such transport and the equipment they should carry so as to minimize the risks to the ship, its crew and to the environment, having regard to the nature of the products carried. The IBC Code lists chemicals and their hazards and gives both the ship type required to carry that product as well as the environmental hazard rating. The products may have one or more hazard properties which include flammability, toxicity, corrosiveness and reactivity.

The IBC-Code includes substances and mixtures and identifies safety and pollution hazards. The hazard identification data are the name the PNS and the pollution category:

- Category X: Noxious Liquid Substances which are deemed to present a major hazard and are therefore prohibited from being discharged into the marine environment;
- Category Y: Noxious Liquid Substances which are deemed to present a hazard and therefore there is a limitation on the quality and quantity of the discharge into the marine environment;
- Category Z: Noxious Liquid Substances which are deemed to present a minor hazard and therefore there are less stringent restrictions on the quality and quantity of the discharge into the marine environment; 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 hazards when discharged into the sea.

The IBC-pollution categories are based on the GESAMP[2]. GESAMP is an advisory body consisting of specialized experts nominated by the Sponsoring Agencies[3]. GESAMP provides scientific advice concerning the prevention, reduction and control of the degradation of the marine environment and elaborated more than 850 GESAMP profiles, which provide a “hazard profile” as an alphanumerical fingerprint of each substance or mixture.

The hazard evaluation procedure is in line with the GHS[4] and REACH[5]. The criteria are:

- Bioaccumulation and Biodegradation

2 GESAMP Reports and Studies 64, Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships, 2nd Edition, 2014

3 (IMO, FAO, UNESCO-IOC, WMO, IAEA, UN, UNEP, UNIDO, UNDP

4 Globally Harmonized System of Classification and Labelling of Chemicals of the United Nations

5 European regulation concerning Registration, Evaluation, Authorisation and Restriction of Chemicals

- Aquatic toxicity
- Acute Mammalian Toxicity
- Corrosion and Long term health effects
- Interference with other uses of the sea

The hazard identifications data are the PNS.

2.1.3 The International Maritime Solid Bulk Cargoes Code (IMSBC Code)

Hazards associated with the shipment of solid bulk materials are generally classified under the following main categories:

- Structural damage due to improper distribution of the cargo, during and after loading;
- Loss or reduction of stability during the voyage, either due to a shift of cargo or to the cargo liquefying under the combined factors of vibration and motion of the vessel; and
- Chemical reaction such as spontaneous combustion, emission of toxic or flammable gases, corrosion or oxygen depletion.

The Code’s three cargo groups are:

i. Group A - cargoes which may liquefy
ii. Group B - cargoes with chemical hazards
iii. Group C - cargoes which are neither liable to liquefy nor possess chemical hazards.

It should be noted that some bulk materials may fall into both Group A and Group B. Bulk materials of group B may be deemed to be hazardous by virtue of the fact they have been classified as a dangerous good under the IMDG Code or it has been determined that they may be Materials Hazardous in Bulk (MHB). It should not be assumed that materials deemed to be MHB pose less of a risk than those with a UN number.

The hazard identifications data are the PNS.

2.1.4 The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code)

The purposes of the code is to provide an international standard for the safe transport by sea in bulk of liquefied gases and certain other substances, by prescribing the design and construction standards of ships involved in such transport and the operational procedures and equipment they should carry so as to minimize the risk to the ship, its crew and to the environment, having regard to the nature of the products involved.

2.2 Identification of hazardous substances

Industry stakeholders (manufacturers, shippers, freight forwarders, logistics companies) are responsible for providing the relevant HNS information, including where appropriate, the Material Safety Data Sheets (MSDS) and other legally required dangerous goods transport documents or dangerous goods manifests to the ship reporting parties

Ship reporting parties (masters, ship agents, and ship operators) are responsible to ensure that the HNS information received from the industry stakeholders is transmitted correctly and accurately to the Member States Authorities. The shipper of dangerous goods is obliged to supply the dangerous goods transport document. The IMO has developed a standardized form for Dangerous goods, the IMO Dangerous Goods manifest[6]. It contains among other data the PSN, UN-number, class and classification as marine pollutant. The declaration of dangerous and polluting goods is regulated by European / national legisaltion, and registered by computer based information systems.

However the nomenclature used in marine transport can be unclear. The proper shipping name (PSN) [7] is that portion of the entry most accurately describing the goods in the Dangerous Goods List, which is shown in upper case characters (plus any numbers, Greek letters, "sec", "tert", and the letters m, n, o, p, which form an integral part of the name). An alternative proper shipping name may be shown in brackets following the main proper shipping name [e.g., ETHANOL (ETHYL ALCOHOL)]. Portions of an entry appearing in lower case need not be considered as part of the proper shipping name but may be used.

The PSN may not follow the systematic naming of chemical substances and other well established identification data of chemical substances like the CAS registry number. Furthermore, the naming of solutions and mixtures as well as articles does not often follow in practice a systematic naming of chemical substances approach, although the PSN requires the declaration of the names of the hazardous substances. In this case, the MSDS of the product specify the information on substances and mixtures.

Relevant MS authorities (SSN NCAs, single window, port, maritime, and security authorities) are responsible for receiving and processing HNS information transmitted by the reporting parties.

This information must be requested as quickly as possible by the Response Services.

Commented [d3]: For example the German ZMGS- module "Dangerous goods" offers an option to search for registered ship voyages with dangerous and polluting goods. More specific information is provided by the linked information system on chemicals RESY. Ship owners, charterers and agents can enter their notifications for dangerous and polluting goods easily, according to the "Entering Requirements Ordinance" (AnlBV).

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[6] http://www.imo.org/OurWork/Facilitation/FormsCertificates/Pages/Default.aspx

[7] http://www.unece.org/fileadmin/DAM/trans/danger/publi/unrec/rev14/English/03E_Part3a.pdf

2.3 Physical properties and environmental behaviour of chemicals, released into the aquatic environment

The Behaviour Classification System contained in the Bonn Agreement Counter Pollution Manual classifies chemicals according to their physical behaviour when spilled into the sea. The classification system covers gaseous, liquid and solid chemicals. The main principle of the system is to characterize spilled chemicals as: evaporators, floaters, dissolvers and sinkers.

From this basic categorization and from other details regarding their physical properties, the chemicals are classified in the following 12 property groups.

G	Gas	GD	Gas that dissolves
E	Evaporator	ED	Evaporator that dissolves
F	Floater	FE	Floater that evaporates
		FD	Floater that dissolves
		FED	Floater that evaporates and dissolves
D	Dissolver	DE	Dissolver that evaporates
S	Sinker	SD	Sinker that dissolves

Human populations as well as the marine environment can be exposed to spilled hazardous chemical substances. Nine potential hazards can be distinguished when chemical substances enter the marine environment. The hazards are listed in Figure 5 and described accordingly for each behaviour category. The hazards Aquatic Toxicity, Bioaccumulation and Persistence may be summed up to the hazard Marine Pollutant

Potential Hazards	Behaviour Category	Human Health	Marine Environment
Toxicity inhalation	G/E/F	X	
Explosiveness	G/E	X	
Flammability	G/E/F	X	
Radioactivity	G/E/F/D/S	X	X
Corrosiveness	G/E/F/D/S	X	X
Carcinogenicity	G/E/F/D/S	X	X
Aquatic Toxicity	D/S		X
Bioaccumulation	D/S		X
Persistence	D/S		X

Figure 1: Most relevant hazards of chemical substances within a behaviour category for humans and the marine

2.4 Hazard assessment

When responding to a spill situation it is vital to predict and monitor which hazards are present in each compartment (air, water surface, water column, and seafloor).

2.5 Information tools

2.5.1 GESAMP (including ECBS)

2.5.2 MSDS

A material safety data sheet (MSDS) is an important component of product stewardship and occupational safety and health. It is intended to provide workers and emergency personnel with procedures for handling or working with that substance in a safe manner, and includes information such as physical data (melting point, boiling point, flash point, etc.), toxicity, health effects, first aid, reactivity, storage, disposal, protective equipment, and spill-handling procedures. MSDS formats can vary from source to source within a country depending on national requirements.

Safety data sheets have been made an integral part of the system of Regulation (EC) No 1907/2006 (REACH). The original requirements of REACH for SDSs have been further adapted to take into account the rules for safety data sheets of the Global Harmonized System (GHS) and the implementation of other elements of the GHS into EU legislation that were introduced by Regulation (EC) No 1272/2008 (CLP) via an update to Annex II of REACH.

Free searches of MSDS are available.[8]

2.5.3 MAR-CIS

2.5.4 MAR-ICE

2.5.5 Databases

The OECD eChemPortal allows simultaneous searching of reports and datasets by chemical name and number and by chemical property. Direct links to collections of chemical hazard and risk information prepared for government chemical review programmes at national, regional and international levels are obtained. Classification results according to national/regional hazard classification schemes or to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) are provided when available. In addition, eChemPortal provides also exposure and use information on chemicals.

[8] For example http://www.msds.com/

eChemPortal[9] provides free public access to information on properties of chemicals:

- Physical Chemical Properties
- Environment, Fate and Behaviour
- Ecotoxicity
- Toxicity

The REACH data[10] comes from registration dossiers submitted to ECHA by the date indicated as last update. The Total Tonnage Band is compiled from all the dossiers with two exceptions; any tonnages claimed confidential and any quantity used as an intermediate to produce a different chemical. The Total Tonnage band published does not necessarily reflect the registered tonnage band(s). The information on chemical properties of registered substances is directly accessible via the OECD eChemPortal

3 Risks and risk assessment

3.1 Exposure, monitoring and predictions

Determining the exact location of the discharged substance(s) is one of the first actions to be taken after a release of chemical(s) has occurred. The location of the release and its trajectory as a function of time needs to be determined. Local conditions at the spill site (i.e. weather, currents, wave heights, and water depth) have to be known, because these conditions will determine the fate and effects of a spill at sea.

In the initial stage of an accident where chemicals are involved it is also important to do “back of the envelope” worst case calculations to determine the largest area that can become affected by a harmful/damaging concentration. This is a rough estimate and prediction made on the basis of the first data available in order to establish a first basis for the initial response. Computer models in combination with on scene measurements and/or sampling should verify this calculation at a later stage in the incident as soon as more complete and accurate data becomes available.

Once the dimensions and/or concentrations of the spill are known the impact of the spill can be assessed. The sensitivity of the area between the initial spill and its final destination also determines the seriousness of a spill. Once a spill or package has been localised, concentration measurements for assessing the

[9] OECD http://www.echemportal.org/echemportal/index?pageID=0&request_locale=en

[10] http://echa.europa.eu/information-on-chemicals/registered-substances

potential impact to human beings and/or the marine environment can be executed. A theoretical approach to determining the impact can be done with the help of computer model predictions. Measurements on scene will determine the actual situation

3.2 Safety considerations

Vessel design requirements see EMSA safe platform study.

> The vessel design requirements are described for the scenarios fire, flammable or explosive, health hazard &toxic, cryogenic or gases under pressure, corrosive. Common design features relate to rescue of personnel, Monitoring, appropriate PPE, training /competent persons, recovery of HNS spills into water, Towing arrangements / manoeuvring casualty vessel and enhanced manoeuvrability

Other contents specialized safety equipment, specialized response teams; scientific support

4 Response

When responding to any incident including HNS then the prime function of the responding vessels is the preservation of life. All HNS incidents have basic requirements and the key goals are:

- To assist in the saving of lives
- To provide medical assistance to casualties.
- Mitigate environmental and ecological impacts
- Reduce Loss

4.1 Communication

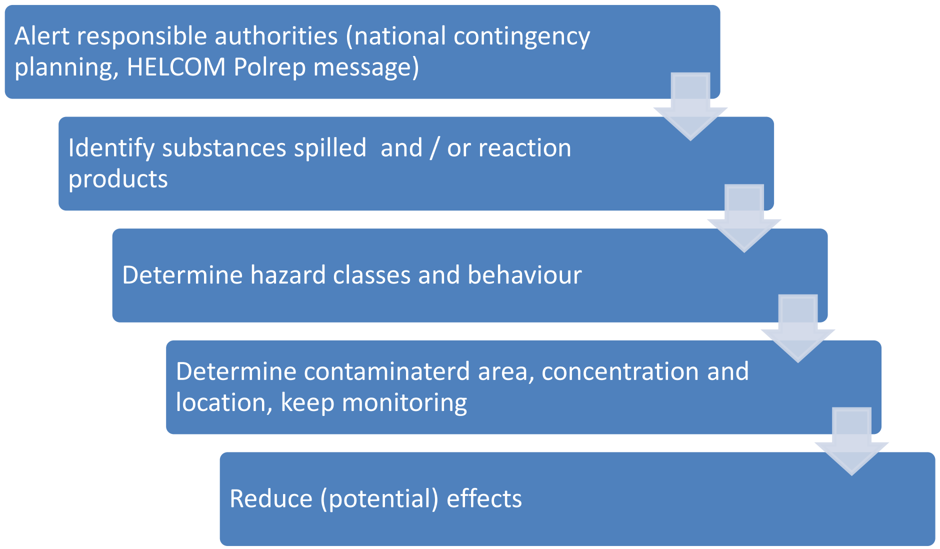
4.2 General approach and general remedial measures

Accurate information must be obtained as quickly as possible about the position of the casualty and other vessels involved, and about the type of substance released and its quantity. This information will need to be confirmed after the first report. Verification of the information can be obtained first by direct communication, via coastal radio station, with the master or pilot of the stricken vessel, and then by local investigation, preferably by helicopter or aircraft with an expert from the competent operational control authority.

Certain measures may be necessary as emergency steps before the situation has been fully evaluated:

Commented [d5]: According to EMSA safe platform study

Commented [d6]: According to HELCOM; EMSA SafeSeaNet Guidelines on Reporting HAZMAT?



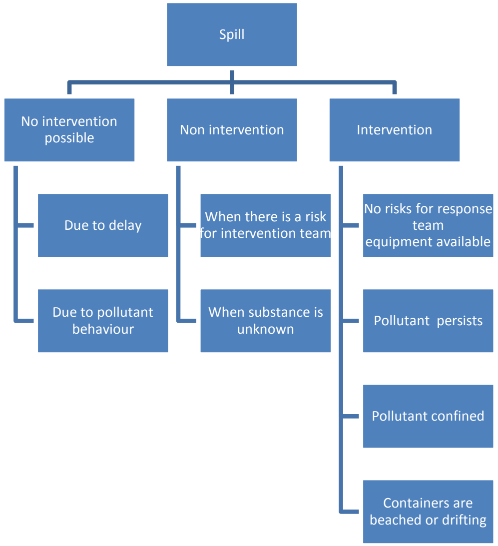
Three general reactions are possible, when an accidental spill has occurred:

In many cases, response action is not technically possible due to the inherent properties and hazards associated with a substance.[11]

No intervention is possible, when there is a risk for the intervention team (explosion, fire, poisoning …) or when the product is unknown. The equipment of the responders - for example response vessels, monitoring devices, personal protective equipment - decides on the applicable methods for remedial measures. To ensure the safety of the responders, no remedial measures should be taken, if the required equipment is not available.

The response reactions, if possible, are presented in the following in form of general remedial measures and in form of decision trees for chemicals with the same behaviour and hazard characteristics (scenarios).

[11] IMO, 2011. Risk of chemical spills at sea. (MEPC/OPRC-HNS/TG 12/5/3)



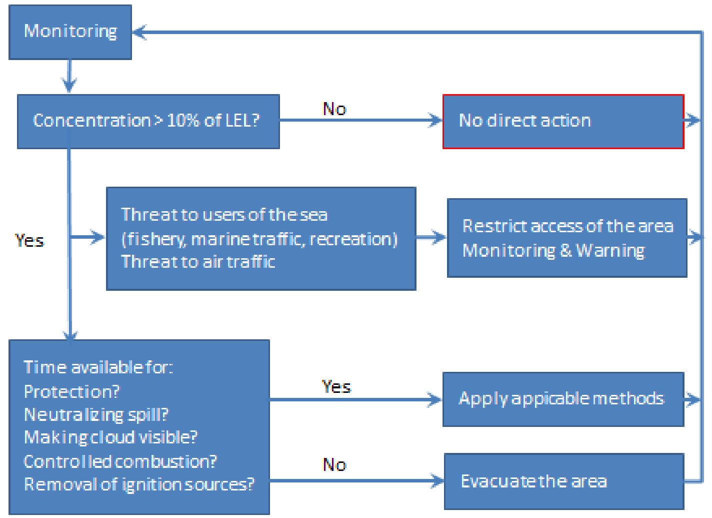
4.3 Chemical releases

The purpose of creating example scenarios is to give the Operational Control body a basis and a starting point for initiating the response. The scenarios are based on some important and representative chemicals grouped according to the main risk to be taken into account in the response operation to an emergency situation at sea. Because most chemicals can cause several different risks in addition to this main risk, these additional risks must also be considered during any response operation.

4.3.1 Gases or Evaporators, toxic or CMR

4.3.2 Explosive gases / vapours

As a rule of thumb, when the concentration of a gas in the air is over 10% of the lower explosion limit value care must be taken in order to avoid an explosion. Gas and vapour plumes are difficult to impossible to combat directly at sea or anywhere else. Response to such plumes is mainly to remove ignition sources and to evacuate the area likely to be affected until the danger has passed. Appropriate computer models to predict the size and trajectory of such a gas cloud can be devised, though direct measurement of concentration is more reliable.



4.3.3 Flammable -floating – substances

4.3.4 Floaters, marine pollutant

4.3.5 Dissovers, marine pollutant

4.3.6 Corrosive Substances

4.3.7 Sinkers, marine pollutant

4.4 Packaged goods

4.4.1 Explosive Substances

4.4.2 Radioactive Substances

4.4.3 Lost packaged goods

5 Annexes

5.1 Endpoints for hazard evaluation; physical properties

Text examples taken from previous version

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5.1.1 Bioaccumulation and Biodegradation

5.1.2 Aquatic toxicity

5.1.3 Acute Mammalian Toxicity

5.1.4 Corrosion and Long term health effects

Irritants - refers to some sort of aggravation of whatever tissue the material comes in contact with. e.g. ammonia, nitrogen dioxide.

chemical asphyxiants - carbon monoxide, hydrogen cyanide, hydrogen sulphide.

Narcotics or Anaesthetics - the main toxic action is the depressant effect upon the Central Nervous System. e.g. - many organics, chloroform, xylene.

Systemic Poisons - the main toxic action includes the production of internal damage e.g. Hepatotoxic agents - toxic effects produce liver damage. eg. carbon tetrachloride.

Carcinogens - agents/compounds that will induce cancer in humans. e.g. benzene, inorganic salts of chromium.

Mutagens - agents that affect the cells such a way that it may cause cancer in the exposed individiual or an undesirable mutation to occur in some later generation. e.g. variety of chemical agents that alter the genetic message.

Teratogens - agents or compounds that that can cause defects in the fetus.

Sensitizers - agents that may cause allergic or allergic-like responses to occur. After an initial exposure to a substance an individual may become sensitized to that substance.

5.1.5 Interference with other uses of the sea

GESAMP, Bonn Agreement

Water solubility S is a central factor determining the environmental fate of a chemical. Water solubility greater than 1,000 mg/l makes a substance highly soluble in water and thus expose pelagic organisms. In comparison, poorly soluble (< 10 mg/l) and hydrophobic substances are typically tightly bound to organic particles and the sediment, and are therefore less available for uptake by pelagic organisms, but can be taken up by bottom feeders. On the other hand, highly water soluble substances are typically readily biodegraded and do not, therefore, have the tendency to accumulate in organisms and food webs (Häkkinen et al. 2010).

Vapour pressure (Pa) (at 20–25 °C) describes a chemical's volatility to the air. Vapour pressure is only used for evaluating liquid substances. Below 0.3 kPa, a floating substance is not considered to evaporate and above 3 kPa evaporation is rapid. A dissolved substance will evaporate if the vapour pressure is higher than 10 kPa. When a chemical is highly volatile, its risks in aquatic environments are greatly reduced, as it will volatize into the air and leave the water system. On the other hand risk for human health could be very high.

In relation to their environmental fate, Henry's law constant H (Pa m3/mol) is also a relevant property, as it characterises the partitioning of a substance between air and the aquatic phase ("evaporation from water"). A Henry's law constant greater than 100 Pa m3/mol means that the substance evaporates extremely easily; values between 1 and 100 Pa m3/mol indicate that the substance evaporates relatively easily, and values lower than 10^{-2} Pa m3/mol indicate that the substance does not evaporate well (Nikunen & Leinonen 2002).

Density (kg/l) is also an important factor determining the final fate of a substance in the aquatic environment. When a substance has a density lower than that of sea water (1.025 g/l at 20°C), it will float, whereas a substance with a greater density than that of sea water will sink (presuming that the compound is neither highly volatile nor water soluble) (GESAMP 2002).

Viscosity (cSt) is a property of liquids. Viscosity determines a substance's resistance to flow, and floating substances with a viscosity greater than ca. 10 cSt (at 10–20 °C) have a tendency to form persistent slicks on the water surface (GESAMP 2002). Besides centistokes (cSt), other units, such as Pa.s (Pascal-seconds) and poises (P), can be used for viscosity as well.

Flammability means that chemical ignites either spontaneously or in the presence of another heat/energy source. The flammability of liquid is determined by chemicals vapour pressure and/or flash point. Flammable liquids to which the most of the heavily transported chemicals in the Baltic Sea are belonging, are characterized by low boiling and flash points. Some chemicals might also catch fire spontaneously in contact with air (ITOPF). The explosive chemical, in turn, becomes unstable under certain conditions, for instance, in the presence of heat, friction, impact, static electricity or when releases its stored or pressurized energy. Flammable and explosive chemicals include: a) Oxidising chemicals; b) Explosives; c) Flammable liquids; d) Highly flammable liquids e); and Extremely flammable liquids and gases (including liquefied petroleum gas and natural gas) f) Other flammable liquids (with flashpoints between 55° and 100°C) g) Chemicals which react violently with water (R14 and R15). Explosions can be followed by shockwaves, fire and heat. Major damage could occur if the energy released cannot be dissipated immediately. For instance, the heating of contained, compressed liquefied gas can lead to the rupture of the container due to

Commented [WNO8]: Abbreviation may not be necessary here, although it does not harm to keep them, or include all in the end in an annex.

overpressure following the boiling of the liquid inside. The instantaneous release can be developed into a large flammable cloud generating flash fire, fireball or a vapour cloud explosion. The lower and upper exposure limits (LEL and UEL) define the range in which a gas or a vapour in air is capable of igniting in the presence of ignition source.

Oxidizing chemicals are not necessarily combustible, but by providing oxygen may cause to the combustion of other material. Nitric acid is example of this kind of strong oxidizing agent that can react violently with organic materials.

Corrosive chemicals can irreversibly damage another material or substance with which they come into contact.These includes living tissues like skin, eyes and lungs and also materials like response equipment and cargoes.

In turn irritant chemical may be harmful to health damaging and causing inflammation to the skin and mucous membranes.

Reactivity…Chemicals may react with e.g. fuel oil, other substances, water or air in many ways including decomposition, corrosion, oxidation/reduction or violent polymerization reaction. Knowing the reactivity of chemical in question has a major importance since these reactions can cause heat and flammable, corrosive or toxic gases (ITOPF). Certain gases might react with oxygen present in the air and ignite and explode. Their Lower Explosive Limit (LEL) and Upper Explosive Limit (UEL) determine the concentrations in air allowing these reactions and these must be known. For ammonia explosion can be happened if there is 15.5 – 26.2 % ammonia in the air.

5.2 Discussion of Baltic Sea transport data evaluated by hazards (taken from ex 2.5. Explanation of hazards, exposure and risks)

The chemicals handled in greatest quantities in the Baltic Sea ports are methanol, sodium hydroxide solution, methyl tert-butyl ether (MTBE), xylenes, pentanes, ammonia, phosphoric acid, sulphuric acid, phenol, and ethanol and ethanol solutions (Posti & Häkkinen 2012). At least hundreds of thousands of tonnes of all these substances are handled annually – some of the volumes even amounting to over 1 million tonnes per year. The majority of the most frequently handled substances belong to MARPOL's pollution category Y, meaning that they are of a moderate hazard if released in the marine environment. Only MTBE, ethanol and ethanol solutions are category Z substances, i.e. the hazard arising from them, according to MARPOL, is only minor. Based on the GESAMP evaluation, the IMO has set up four different hazard categories: X (major hazard), Y (hazard), Z (minor hazard) and OS, i.e. other substances (no hazard) (IMO 2007). More than 80 % of all the chemicals transported in the Baltic Sea are classified as belonging to the Y category. Hazards to the environment can vary a lot depending the chemical in question and impact can be acute or long-lasting. Cargo outflow may lead to mortality of certain species, contamination of coastline or disturbances to local amenities, etc. Most shipping accidents have local impact on the environment, but accidents may have also wider effects. This can happen via affecting components of the ecosystem that are significant for the whole region. For example, habitats, spawning grounds, or wintering areas are this kind of key components. Furthermore, the environmental effects of a spill depend greatly on the time and place of the spill and also other factors. This means that different spills of the same size can also have different effects on the environment.

Ecotoxicity of the chemicals depends on bioaccumulation, persistence and acute/chronic toxicity (Häkkinen et al. 2010, 2012, 2013). Based on the analysis of chemicals transported in the Baltic Sea, Häkkinen et al. (2013) stated that nonylphenol is the most toxic of the studied 15 heavily transported chemicals and it is also the most hazardous in light of maritime spills. The chemical is persistent, accumulative and has a relatively high solubility to water. Nonylphenol is actually transported in the form of nonylphenolethoxylates but it is present as nonylphenol when spilled into the environment, and in the aforementioned study the worst case scenario was evaluated. Other very hazardous substances were sulphuric acid, ammonia, phenol and coal tar (Häkkinen et al. 2012, 2013). In case of a major accident happening close to nuclear plants, many industrial chemicals could be present in concentrations high enough to impact water biota resulting in e.g. mass deaths of fish

6 Glossary

To be filled