MARINER

Enhancing HNS preparedness through training and exercising

TITLE OF THE DOCUMENT

Task D: ANNEX II: PROTOCOLS FOR RESPONDING TO HNS SPILLS AT SEA

Action D.1&D.2

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1. Objective

This guide aims to help responders to properly intervene on HNS spills from an antipollution ship. It includes response options highlighting the most relevant actions that have to be taken into account when dealing with this kind of incidents.

Notice that **radioactive** HNS are not included in this guide.

2. What HNS means?

"Hazard and Noxious Substance", or HNS, has been defined according to the "*Protocol on Prepardness, Response and Coopertion to Pollution Incidents by Hazardous and Noxious Substances, 2000*", the OPRC-HNS Protocol, as any substance other than oil which, if introduced into the marine environment, is 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. "HNS" therefore includes hazardous or dangerous chemicals, but also includes many other substances which might be regarded as relatively harmless in other circumstances.

3. How are HNS classified?

According to the 2010 HNS Convention, HNS are included in one or more lists of IMO conventions and codes designed to ensure maritime safety and pollution prevention. The number of substances included in these lists is enormous and for this reason there is no single list or agreement that integrates them all. The diversity of existing substances, the way in which they are transported by sea, their behaviour when being discharged into a marine environment, or the potential diversity of response techniques in case they are discharged, has promoted the elaboration of multiple taxonomic classifications based on approaches different individuals. Because the response to the spilling of these substances at sea is dependent on multiple aspects collected in different classifications, it is not possible to adopt a single classification when establishing response protocols.

Figure 1 shows the main codes used for HNS classification depending on how they are transported and Conventions that apply in each case.

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Figure 1: International codes for chemicals carried by ships

Two classifications needs to be highlighted related to the potential threat to human health and to the marine environment caused by the release of HNS into the sea. That what includes substances on Category X, Y, Z or OS depending of their hazardousness and that what evaluate the GESAMP procedure based on the bioaccumulation, biodegradation and aquatic toxicity of the substances.

Taking into account that the present document is focused on the response protocols when a HNS is spilled, special attention deserves the nine major classes of HNS described in the International Maritime Dangerous Goods (IMDG) Code. Table 1 shows the properties to be considered in each case.

Class	Types of substances and articles	Properties to be considered
1	Explosives	Risk for mass explosion, hazardous gases or projection, sensitivity to water or impact
2	Gases compressed, liquefied, or dissolved under pressure	Flammability, toxicity, oxidizing effects, corrosiveness
3	Flammable liquids	Flash point, toxicity, corrosiveness, solubility in water
4	Flammable solids	Sensitivity to drying, carbon dioxide or water
5	Oxidizing substances	Risk of explosion, type of packaging
6	Poisonous repugnant and infectious substances	Type of toxicity, flammability, sensitivity to water
7	Radioactive substances and articles (Not included in this guide)	Level of activity, package design
8	Corrosives	Level of corrosiveness, flammability, flash point
9	Miscellaneous substances and articles	

Table 1: Classes of HNS according to IMDG Code

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In spite of some specific guides to deal with several HNS have been developed, the huge amount of different HNS that are transported by sea makes individual response sheet for each product unimaginable. It is deemed more suitable to approach the response by grouping them depending on their behaviour when released into the marine environment. In this sense HNS depending on their physicochemical properties will evaporate immediately, evaporate rapidly, float, dissolve or sink or simultaneously present different behaviours depending on the environmental conditions. Figure 2 shows the different behaviours a substance ca have when released. This approach has been defined in the framework of Bonn Agreement with the Standard European Behaviour Classification (SEBC).

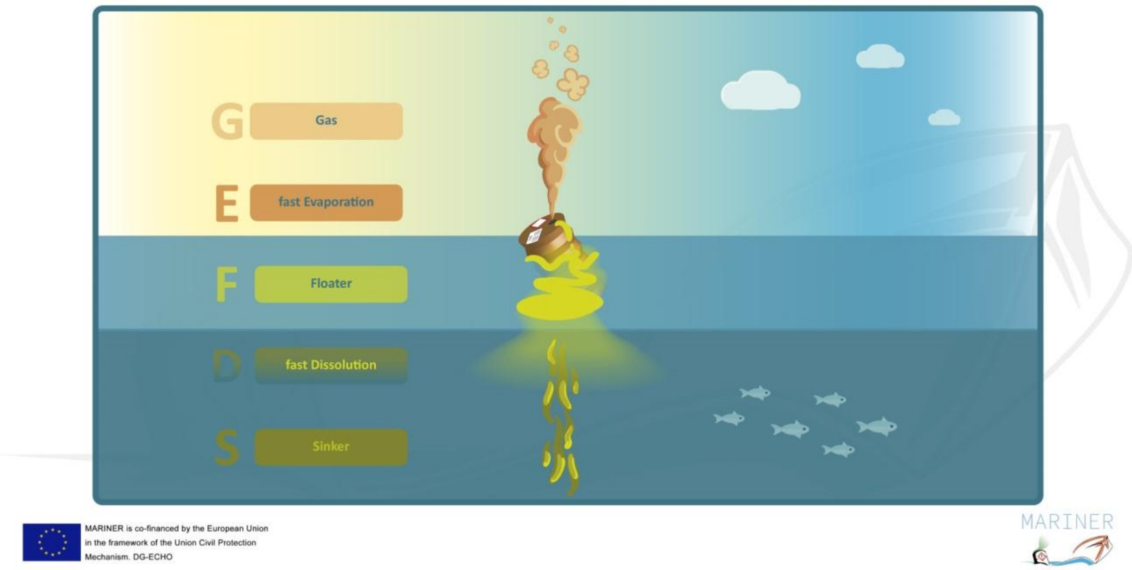

Figure 2: Main behaviours defined by the SEBC

4. How can HNS affect to responders?

Exposure to hazardous substances can affect the body in many different ways. Skin contact, inhalation and ingestion can cause damage. Moreover, HNS can cause short- and long-term health problems. They can cause serious ill health including cancers, dermatitis and asthma. The hazards associated with a particular substance are dependent on its inherent properties and its fate in the marine environment.

The Safety Data Sheets (SDS) will provide information on the hazards of the substances involved as well as indicate possible incompatibilities or reactivity with water or other substances if more than one is involved. When responding to an incident where HNS are involved, response personnel must be aware of which are the main exposure routes. Figure 3 shows how a contaminant can reach different parts of human body.

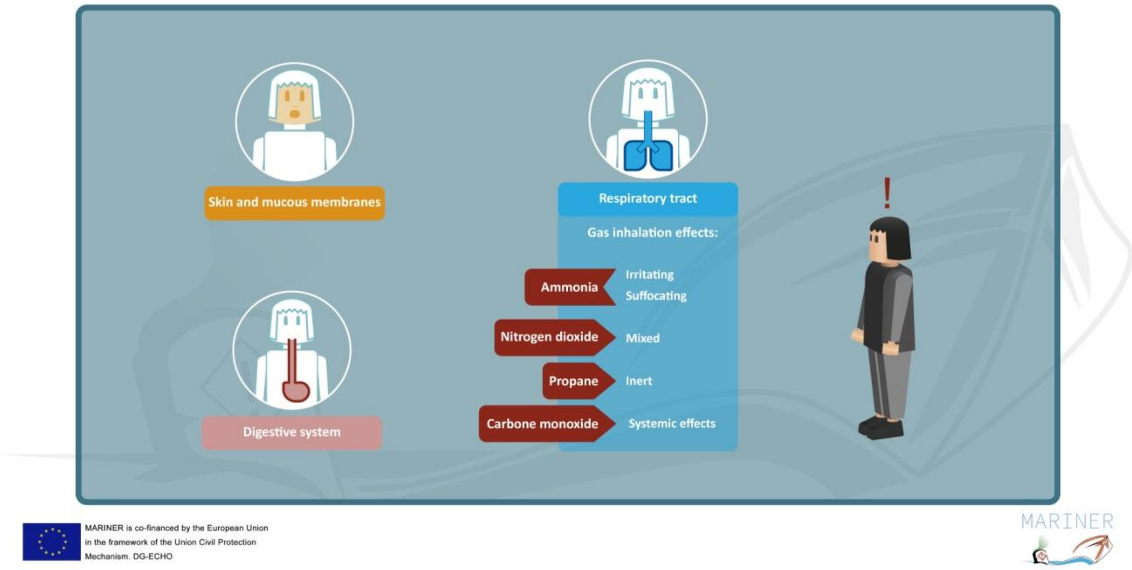

Figure 3: Main ways of HNS penetration in human body

5. Maritime transport of HNS

Maritime transportation of chemicals has grown considerably in the last few decades; worldwide approximately 2,000 different chemicals are transported by sea. HNS cargoes can be carried at sea either in bulk or packaged form. There are many different types of ships which carry HNS:

- bulk carriers that transport bulk cargos as grain, ores, vegetable or fish oil and others. They can be recognised by its large box where the cargo can be transported in either liquid or solid form

- ships that transport HNS in packages, as containerships that are specialised carriers that transport goods in containers (box-type); general cargo ships (e.g. RO-RO or ferries) that usually carry cargo in relatively small consignments as boxes, drums and others and ro-ro ships that are adapted to facilitate the quick loading and discharge by using road trailers or rail tank cars

- ships that transport HNS in liquid or gas, as chemical tankers that are specialised class of tankers designed to carry the most dangerous of liquid chemicals, the product tankers prepared to carry a broad range of chemicals and the gas carriers built to carry gas in either a pressurised or refrigerated form.

Figure 4 shows some common types of vessels which carry HNS and the increase of them during the last years.

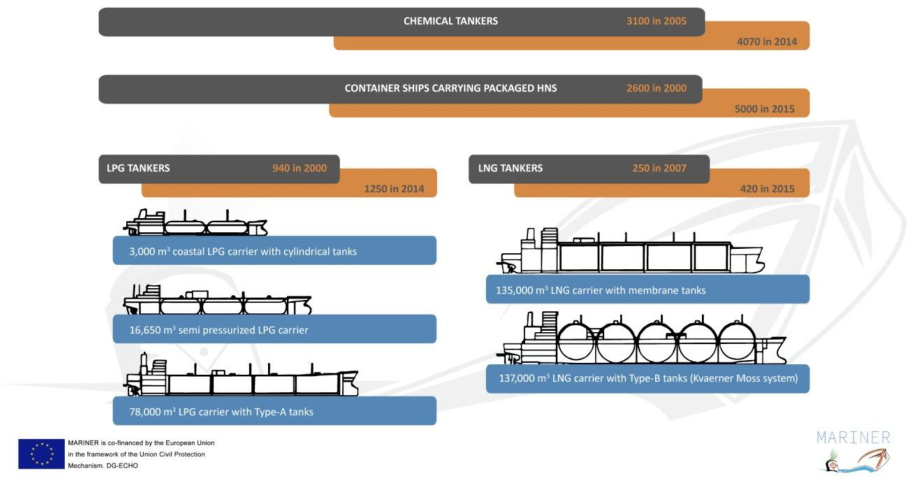

Figure 4 Ships that transport HNS by sea

6. Response to HNS

As it occurs with oil spills, the main objectives of an HNS spill response are in order of priority: protect human health and safety, minimise environmental impacts, mitigate impacts on amenities and restore the environment as soon as possible to pre-spill condition.

Taking into account those aims, an appropriate response must follow several steps consecutively:

6.1. First steps before responding operations

Actions to protect:

- evacuate the incident zone and/or confine from toxic cloud exposure
- cut ignition sources out
- stop the leakage (only if possible without risk)

Actions to alert:

- Immediate alert to competent authorities
- Urgent alert on the incident zone
- Alert the responder teams

Actions to respond:

identify substance and define spillage location

estimate volume spilled and contaminated zone

delimit danger area and control de access

assess the hazards and risk of HNS spill response

6.2. Salvage actions

Although salvage actions are not the objective of this document, they should be considered as a priority when responding to an HNS incident.

HNS cargoes require more specialist salvage operations than other cargoes. The practicality of any salvage response will depend on the prevailing situation of the damaged vessel, several considerations has to be taken into account as if it is on fire, or it is still afloat and it might be towed, if it is grounded or if it has sunk. Considerations about the cargo are also critical as if it is intact and it might be removed from the damaged vessel and transferred onto another suitable vessel or if it has been partially or totally released to the environment interfering into the salvage operations.

6.3. Actions to respond to HNS incidents

Most crew on board of ships that transport HNS are fully aware of the potential risk that those substances can suppose and usually they are well prepared to deal with them as part of the specific emergency plans for each cargo. In this sense actions that can be taken by the crew during the first moments are critical for reducing the potential consequences of an incident. Those actions include closing valves, transferring cargo, changing the position of the ship to take explosive or toxic vapours away, moving to less vulnerable areas away from population centres or sensitive environmental resources.

Once the HNS has been released into the environment opportunities to respond are quite limited when compared with oil spills. Techniques applicable to oil spill response may be suitable for some chemical substances that can be safely contained and/or physically removed. The range of the behaviour for HNS is extensive, especially when more than one chemical is present. Moreover, HNS can react between them and with the environment originating new products that must to be taken into considerations.

There are three available categories of responding: forecasting, monitoring and combating.

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6.3.1. Forecasting HNS spill movement

Several computer models and modelling systems exist by which an operator, after some education and training, can elaborate a forecast of the spill's future fate. It needs to be notice that the reliability of this forecast depends fully on the model's construction and validity, how accurate are all input data and how professional the model is run. In these sense some of those limitations can lead on a misleading picture of the drift.

Different methods can be used to forecast the spread of HNS in air, on water surface or in a body of seawater. The first one is applicable to gases and to any liquid, volatile enough to produce vapour cloud. The second one is applicable to HNS that mainly behaviour as floaters and the third one to HNS that dissolve when released into waters. All these forecast will be influenced by different ocean meteorological conditions, as temperature, wind direction and intensity, hydrodynamic conditions, currents and so on. In all cases, these predictions can provide to the responder information about which are the different areas of health risk, fire/explosion risk depending on the specific HNS. This information is critical to establish the areas of exclusion or response where some actions can take or not place.

Figure 5 shows examples of model outputs. It needs to be notice that in marine incidents the movement of the contaminant source could represent an additional inconvenience when estimations of distances are carried out, forcing modellers to constantly update their prediction.

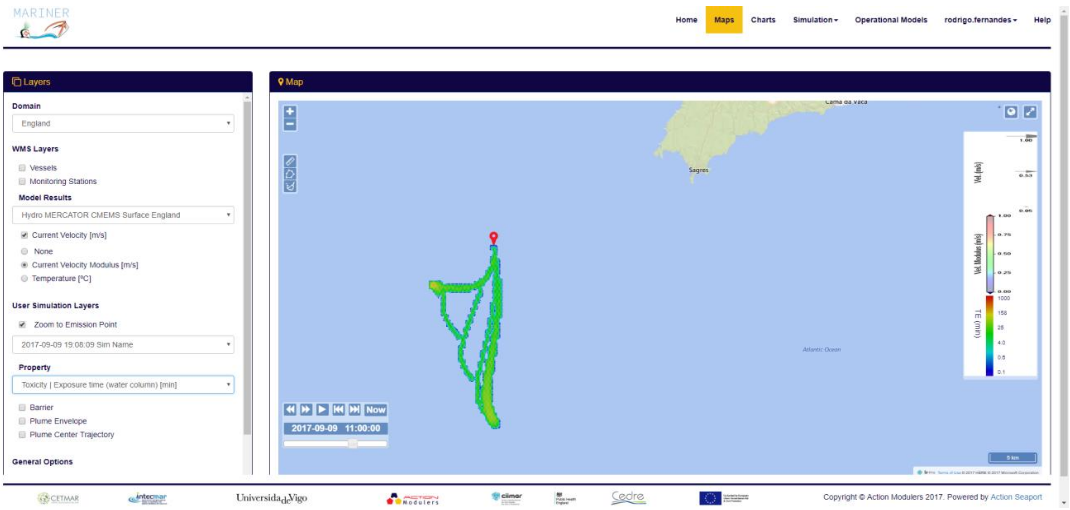

Figure 5: Output of the modelling tool developed in the framework of MARINER project

6.3.2. Monitoring HNS spill

When HNS is spilled, it is crucial to monitor the air the water and the sediment for presence or concentrations of hazardous substances. The aim of monitoring is to assess both toxic and fire/explosion hazards, map the area where unprotected personnel should be evacuated, judge the appropriate level of personal protection equipment for response personnel.

Values of the instruments used to monitor can be used directly for identifying risk areas or to check risk areas that are already defined according to forecasting models outputs.

When HNS is spilled, depending on whether the HNS is, it is crucial to monitor the air for concentrations of hazardous substances, presence or concentration of HNS in the water column, on the surface or on the seabed. For those actions numerous kits of detection or more sophisticated portable equipment is available that can be used to monitor the hazardous substances. It is important to point out that such action is not always technically possible or too risky.

Monitoring can also be carried out using other techniques as aerial reconnaissance, satellite imagery, echo sounders or drifting buoys that drift within the contaminant giving the position in a continuous way. Figure 6 shows some examples of drifting buoys used to continuously locate the spill of a floating product.

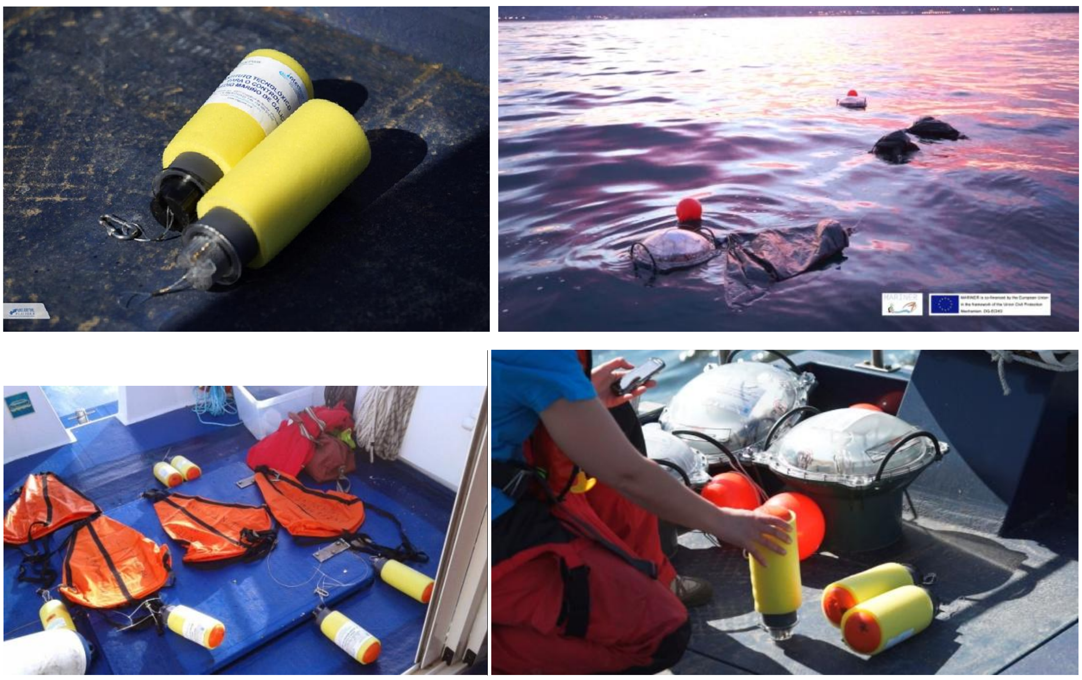

Figure 6: Example of drifting buoys

6.3.3. Combating HNS spills

During response operations some issues need to be considered:

- only the responders team should be on site

- always be aware of the weather forecast (wind and rain) and the meteo-oceanic conditions forecast (water temperature, swell and currents)

- consider an UNKNOWN substance as DANGEROUS

- make sure people on site are safe

- monitoring clouds vapour (toxicity, corrosivity, carcinogenicity, explosivity, flammability, radioactivity), the drift of the slick, containment and recovery options, the spread of the contaminant in the seawater column

- personnel must always wear the appropriate personal protective equipment depending on the substance and the exposure route that has to be protected. It can be:

Level A: a fully encapsulating chemical protective suit, self-contained breathing apparatus

Level B: A chemical resistant suit with an external SCBA

Level C: chemical resistant clothing, gloves and boots, full-face mask air-purifying respirator

Level D: the lowest level of protection, basic work clothing, gloves and safety shoes.

Type 1 (EN 943)	Hermetic to gaseous chemical products or in vapour form. They cover the entire body, including gloves, boots and respiratory protective equipment. All of them are constituted by non-breathable materials and with resistance to permeation. They are subdivided into: 1a. They wear the respiratory protection equipment inside the suit 1b. They wear the respiratory protection equipment on the outside of the suit 1c. They are connected to a breathable air line
Type 2 (EN 943)	They are like those of type 1b but their seams are not watertight. All of them are constituted by non-breathable materials and with resistance to permeation
Type 3 (EN 14605)	They have hermetic connections to liquid chemical products in the form of a pressure jet. All of them are constituted by non-breathable materials and with resistance to permeation
Type 4 (EN 14605)	They have hermetic connections to liquid chemicals in aerosol form. They can be constituted by breathable or not materials, but they offer resistance to permeation
Type 5 (EN 13982-1)	They have hermetic connections to chemical products in the form of solid particles. They are made of breathable materials and the level of performance is measured by the resistance to penetration of solid particles
Type 6 (EN 13034)	They offer limited protection against small spills of liquid chemicals. They are made of breathable materials and the level of performance is measured by the resistance to penetration of liquids

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- once the response operations have been chosen depending on the principal behaviour of the substance, response actions must always include the appropriate continuous monitoring of spill evolution

6.3.4. Response to EVAPORATORS/GAS

6.3.4.1. Monitoring of the gas cloud:

- directly monitored by using appropriate equipment to delimitate safety zones as those used for trace gas (gas detection tubes, portable gas chromatographs, photoionization instruments, semiconductor instruments, IR trace gas detectors or mobile mass spectrometers, etc.); equipment used to determine flammability and explosiveness (explosive meter and combustible gas detector) or equipment to detect oxygen-deficiency (chemical celloxygen meters) and UAVs

- forecasted gas cloud behaviour by using emergency software. As most concern for health and safety lies with gases and evaporators, several air dispersion models have been developed as ALOHA or CHEMMAP to aid decision making and provide conservative estimates of safe distances for protection of the population and responders. In the framework of MARINER project a modelling tool has also been developed.

6.3.4.2. Response operations:

- seal the breach with specific mechanical or pneumatic tools, used for gas tanks but AVOIDING SPARKS is a crucial requirement for this operations

- re-condense leaking gases by covering the container with a flat tarpaulin collecting the jet stream with a tarpaulin made as a funnel or cone These both options are difficult to practice on board, being more adequate for harbours and shoreline lost containers - use water spray or mist to wash down water soluble gas clouds cooling down hot surfaces, to avoid thermic equipment, suppress spark or flame formation

stop, steer or disperse gas clouds AVOID using water on COLD liquefied gases

Attention needs to be given to the fact that containment and recovery of polluted water must be taken into consideration in order to avoid them to cause environmental damage by contaminated run-off. The consequences of using water sprays on the stability of the casualty should also be considered.

- mark the cloud with specific substances to make it better

Figure 7 shows an example of the use of a water curtain to avoid gas dispersion

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Figure 7 Water curtain for gas bringing down

6.3.5. Response to FLOATERS

6.3.5.1. Monitoring the contaminant drift:

- directly monitored by using appropriate equipment to delimitate safety zones as those used gas clouds in those cases where the substance evaporates producing vapours or by drifting buoys displayed into the spill to continuously follow the drift

- forecasted spill drift by using emergency software as MOHID or CHEMMAP

6.3.5.2. Response operations:

- reduce the vaporisation process and the risk of fire and explosion by applying curtain or foam using fire fighting equipment and contain and recover the mixture

- recovering floating substances of high viscosity

- distribute sorbents over the floating spill on the water surface and recover the sorbent-spill mixture

- use conventional oil response equipment as skimmers or booms to contain and recover the substance

- if ALLOWED, disperse the floating spill by using chemical dispersants or mechanical dispersion

Sometimes HNS that are transported in packages as drums that contain chemical substances which density is lower than seawater's, can act as floaters (independently of the behaviour of the substance when it is free released into the seawater) when released, drifting in the surface or appearing stranded on the beach. In those cases the encapsulation of the package seems to be the best action. Figures 8 and 9 show some examples of this method.

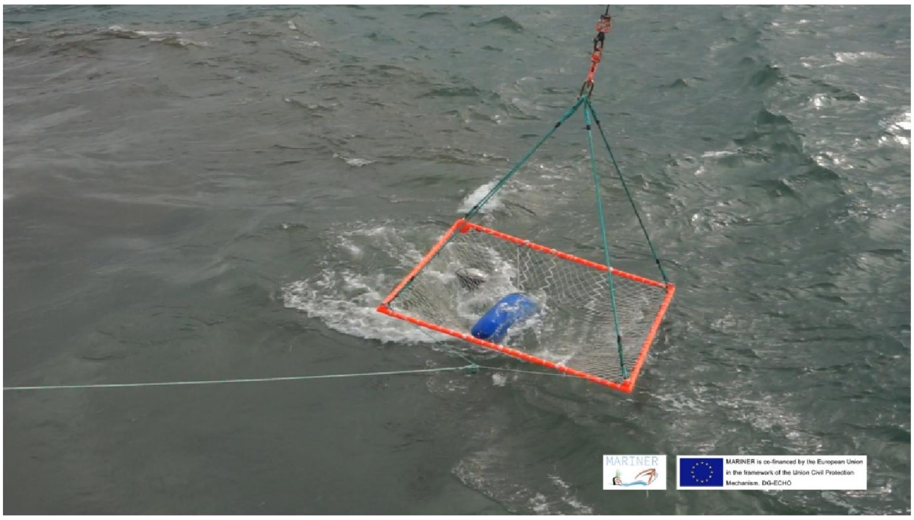

Figure 8: Recovering floating HNS drum from the sea water

Figure 9 Training the encapsulation of floating HNS drums

6.3.6. Response to DISSOLVERS

6.3.6.1. Monitoring of the contaminant drift:

- directly monitored by using appropriate equipment as water quality in situ measurement sensors (portable CTD meter, UV- spectruofluorimeter; pH meter, etc.), see figure 10 or by drifting dragged buoys displayed into the spill to continuously follow the drift. The HNS will form a growing plume, which if invisible could be difficult to track.

- forecasted spill drift by using emergency software as MOHID or CHEMMAP

- colour the slick by using innocuous substances, see figure 11

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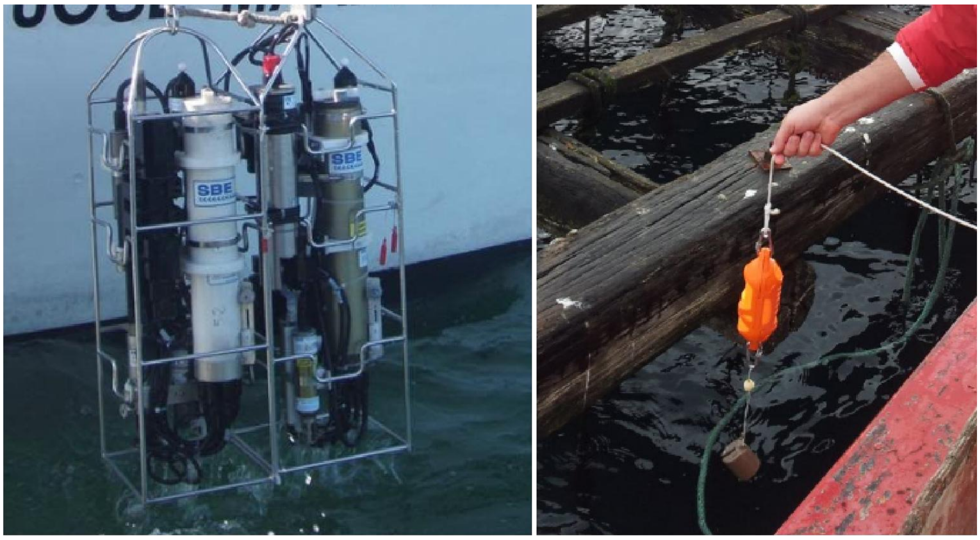

Figure 10: Water monitoring using Seabird 25 CTD and Castaway CTD (source Intecmar)

Figure 11: Coloured slicks (Source: Intecmar)

6.3.6.2. Response operations:

- neutralise the spill by using neutralising agents, in cases of acid or base chemical spills. Two neutralising agents can be used to neutralise pH variations: sodium carbonate for acids and sodium di-hydrogen-phosphate for base spills.

- purificate contaminated water by using filters (adsorption process, ionic exchangers resins, flocculation agents)

All these techniques are only possible in shallow waters where the HNS may be confined. The effectiveness of these treating agents will depend on the ability of the product and the HNS to interact together which is rarely the case.

In all cases, the agents should be RECUPERATED

6.3.7. Response to SINKERS:

6.3.7.1. Monitoring the contaminant movement:

- directly monitored or sampling by direct observation on the sea bed using sub aquatic equipment (divers, Remotely Operated Vehicles (ROVs))

- indirectly by using remote sensing (echo sounders)

6.3.7.2. Response operations:

-recover sunken spills on the bottom by dredging techniques as airlift pneumatic dredges, trailing suction hopper dredges, dregs with suction pump or other mechanical dregs. However, dredging is likely to generate large quantity of potentially contaminated dredged material and care need to be taken to ensure proper containment and disposal of this.

- recover HNS contained in packages by releasing or pumping into other containers and this has been achieved primarily by the assistance of ROVs

- cover contaminated sediment by dumping heavier clean sediment on top of the contaminated sediment in order to prevent the HNS from being spread further in the environment. However, this technique is not desirable since the contaminant remains into the sediment.

Figure 12: NRBQ equipment used for sub aquatic protocols

6.4. Decontamination and waste management

Decontamination operations are of critical importance if we do not want to make the situation worst. Once the personnel or the equipment have been in contact with an HNS, they need to be decontaminated in order to avoid the contamination of clean areas. There are numerous equipment and products that can be used to decontaminate.

Decontamination process must be sized prior intervention takes place.

Figure 13: Decontamination units

Wasted generated in both, response operations and decontamination actions, must be managed by appropriate companies.

7. Conclusions

Planning and conducting responses to spills of HNS need to be much more incident-specific and less generic than for oil spills. Any response to a spill of HNS requires a good knowledge of what kind of hazards does the substance pose to the human health and to the marine environment. The key difference when undertaking an initial assessment for HNS incidents, as compared with oil, is the timing.

The challenge for responders is to focus on the most important health and safety hazards, especially in complex incidents involving more than one chemical.

HNS that float could be the most feasible to respond as such situations call on similar methods and procedure used for well known oil spill response.

HNS that dissolve or distribute in the water column such as acids, bases and alcohols are of difficult treatment, moreover if the water body is large and constantly moving.

HNS that are heavier than seawater have the potential to contaminate large areas of the seabed making recovery difficult, time-consuming and expensive.

Decontamination and waste management operations are critical in order to avoid the spread of the contamination to larger areas.

With some HNS spills, no response will be advisable because the potential hazard to responders may outweigh all other considerations, or because it may be impossible to respond within a feasible time period. So, the DO NOTHING approach, where the situation is kept under observation as it evolves, is sometimes the most appropriate approach.

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