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# Introduction

The volume of chemicals transported by sea continues to increase year by year and, as a result, there is growing international awareness of the need for the development of safe and effective contingency arrangements for responding to chemical spills. However, the wide variety of chemicals, their varying physical properties and different behaviour once spilt and the potential for effects on human health and the marine environment mean that preparedness and response arrangements for chemical spills are far more complex than for oil spills.

This paper provides an introduction to the issues involved in responding to chemical spills and addresses the range of hazards present, the behaviour of chemicals when spilt at sea and briefly reviews available response options.

## What are chemicals?

The term 'chemical' encompasses every substance known to man. However, not all chemicals transported by sea are considered hazardous but those that have been termed 'hazardous and noxious substances' (HNS). The OPRC–HNS Protocol<sup>1</sup> defines HNS as “any substance other than oil that, 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”. The hazard associated with a particular chemical is dictated by its inherent properties and, as such, HNS may exhibit one or more of the following five properties: flammable, explosive, toxic, corrosive or reactive.

Another definition of HNS, but one that differs widely from that of the OPRC-HNS Protocol, is provided by the HNS Convention<sup>2</sup>. Under that Convention, a substance is classed as HNS if it is included in one or more lists in the International Maritime Organization (IMO) Conventions and Codes listed in Table 1. The Conventions and Codes listed are designed to ensure the safe transport of all types of chemicals. In addition to listing the different types of HNS, they also

<sup>1</sup> Protocol on Preparedness, Response and Co-operation to Pollution Incidents by Hazardous and Noxious Substances, 2000 (see [www.imo.org](http://www.imo.org)).

<sup>2</sup> International Convention on Liability and Compensation for Damage in Connection with the Carriage of Hazardous and Noxious Substances by Sea, 1996. As of March 2012, the HNS Convention is not yet in force (see [www.hnsconvention.org](http://www.hnsconvention.org)).



▲ Figure 1: Chemical tanker.

prescribe design and construction standards for the different ships involved in the transport of HNS, and regulations on the labelling, packing and stowage of chemicals. Radioactive and infectious substances are outside the scope of the HNS Convention and of this paper.

The OPRC-HNS Protocol is designed for preparedness and response and the HNS Convention for compensation. The difference between the two definitions of HNS is significant because each covers cargoes that are not included in the other. For example, the OPRC-HNS Protocol includes cargoes such as coal, cement, various metal ores and grain. The loss of such cargoes can cause environmental

| HNS material         | Conventions & Codes   |
|----------------------|---|
| Oils carried in bulk | Appendix I of Annex I to the International Convention for the Prevention of Pollution from Ships, 1973 as modified by the Protocol of 1978 (MARPOL 73/78)                     |
| Bulk liquids         | Chapter 17 of International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (IBC Code) and also Appendix II of Annex II to MARPOL 73/78 |
| Gases                | Chapter 19 of International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code)  |
| Solids in bulk       | Section 9 of International Maritime Solid Bulk Cargoes Code (IMSBC Code) if also covered by IMDG Code in packaged form  |
| Packaged goods       | International Maritime Dangerous Goods Code (IMDG Code)   |

▲ Table 1: Examples of IMO Conventions and Codes providing HNS lists (see [www.imo.org](http://www.imo.org)).



▲ *Figure 2: Spilt oil and containers floating from a grounded container vessel (image courtesy SMIT).*

damage through smothering and, in the case of grain, its decomposition can also bring about localised high biological oxygen demand and the release of hydrogen sulphide, a toxic gas. Conversely, the HNS Convention covers many of the common non-persistent distilled products of mineral oil, such as kerosene and petrol (gasoline) and also, in some instances, persistent oil, all of which are not covered by the OPRC-HNS Protocol as they fall under the OPRC 90 Convention<sup>3</sup>. Both the OPRC-HNS Protocol 2000 and the HNS Convention cover vegetable oils. The response to spilt oils is covered in the other papers in this ITOPF TIP series, as listed on the back cover.

## Shipping of HNS

Increasing global demand for chemicals used in a wide variety of industries has resulted in rapid growth of the seaborne chemical trade. In 2010, the IMO listed the top 20 chemicals, (excluding crude oil, its liquid products and vegetable oils), carried by sea and most likely to be involved in an HNS incident. This list was developed by gathering data on the volumes of chemicals produced, the most commonly transported chemicals and those most frequently spilt (*Table 2*).

Cargoes of HNS may be transported by sea in two ways: either in bulk (liquids and solids) or in packaged form. Several different types of ship transport HNS, as follows:

- **Bulk Carriers** – carry solids in bulk as un-packaged dry cargoes, for example iron ore, rock phosphate, coal, cement and grain.
- **Chemical, parcel or product tankers** – carry bulk liquid cargoes, the difference being how the tanks are segregated and the type of chemicals carried, for example benzene or styrene (*Figure 1*).
- **Gas carriers** – transport cargoes of liquefied gas under pressure and/or reduced temperatures, namely Liquefied Natural Gas (mainly methane) (LNG) and Liquefied Petroleum Gas (propane and butane) (LPG).
- **Container ships** (*Figure 2*) – carry cargoes of packaged goods in intermodal containers that allow efficient loading and offloading. The size of a container ship is often quoted in TEU (twenty-foot equivalent units), which is the number



▲ *Figure 3: Stranded tanktainers and a container lashed together on a shoreline.*

of standard-sized containers the vessel can carry. A small proportion of the containers shipped are isotanks or 'tanktainers', for carriage of bulk liquids (*Figure 3*).

- **General cargo vessels** – carry smaller consignments of loosely packaged goods, for example on or in pallets, crates, boxes or drums. In terms of ship type these represent the largest category of the world fleet.
- **Roll on-Roll off (Ro-Ro) vessels** – transport road trailers or rail freight rolling stock carrying loosely packaged goods, containers or bulk liquids and solids.

An incident involving a ship carrying more than one HNS, for example, container ships, parcel tankers or Ro-Ro vessels, presents additional complications due to the potential for the various cargoes to mix with each other, as well as with water should individual containers, tanks or trailers become damaged. In particular, identification of the specific contents of a container or trailer and the assessment of the hazards posed may be difficult to accomplish and in some cases, the dangerous goods manifest (*Figure 4*) and stowage plans may not provide sufficient detail to adequately assess the severity of a potential incident.

Even relatively small quantities of HNS may pose a significant risk. As an example, aluminium phosphide (AIP), a widely carried fumigant, reacts with water to produce phosphine (PH<sub>3</sub>), a toxic gas (*Figure 5*). An incident may also involve a spill of bunker fuel or other oil (*Figures 2 and 5*), which may add further complications to the response. If the HNS represents a danger to human health, a response to the spilt oil at sea or on the shoreline may not be possible or may be compromised.

## Behaviour of chemicals in the marine environment

### Physical behaviour

Classifying substances, whether gases, liquids or solids, according to the behaviour exhibited when released into the marine environment, is a useful tool when developing a response strategy. The fate of a substance is determined by

<sup>3</sup> *International Convention on Oil Pollution Preparedness, Response and Co-operation.*

| Rank | Chemical                        | Behaviour                     | Main hazard  |
|------|---------------------------------|-------------------------------|--|
| 1    | Sulphuric acid                  | Sinker/dissolver              | Corrosive / exothermic reaction with water / fumes |
| 2    | Hydrochloric acid               | Sinker/dissolver              | Corrosive / exothermic reaction with water / fumes |
| 3    | Sodium hydroxide / caustic soda | Sinker/dissolver              | Corrosive / exothermic reaction with water         |
| 4    | Phosphoric acid                 | Sinker/dissolver              | Corrosive / exothermic reaction with water / fumes |
| 5    | Nitric acid                     | Sinker/dissolver              | Corrosive / exothermic reaction with water / fumes |
| 6    | LPG/LNG                         | Gas (transported as a liquid) | Flammable / explosive                              |
| 7    | Ammonia                         | Gas (transported as a liquid) | Toxic  |
| 8    | Benzene                         | Floater/evaporator            | Flammable / explosive                              |
| 9    | Xylene                          | Floater/evaporator            | Flammable / explosive                              |
| 10   | Phenol                          | Dissolver/evaporator          | Toxic / flammable                                  |
| 11   | Styrene                         | Floater/evaporator            | Flammable / toxic / polymerisation                 |
| 12   | Methanol                        | Floater/dissolver             | Flammable / explosive                              |
| 13   | Ethylene glycol                 | Sinker/dissolver              | Toxic  |
| 14   | Chlorine                        | Gas (transported as a liquid) | Toxic  |
| 15   | Acetone                         | Floater/evaporator/dissolver  | Flammable / explosive                              |
| 16   | Ammonium nitrate                | Sinker/dissolver              | Oxidizer / explosive                               |
| 17   | Urea                            | Sinker/dissolver              | Irritating   |
| 18   | Toluene                         | Floater/evaporator            | Flammable / explosive                              |
| 19   | Acrylonitrile                   | Floater/evaporator/dissolver  | Flammable / toxic / polymerisation                 |
| 20   | Vinyl acetate                   | Floater/evaporator/dissolver  | Flammable /toxic / polymerisation                  |

▲ Table 2: IMO list of the top 20 chemicals likely to pose the highest risk of being involved in an HNS incident, not including crude oil, liquid distilled crude oil products or vegetable oils (source: MEPC/OPRC-HNS/TG 10/5/4, see www.imo.org).

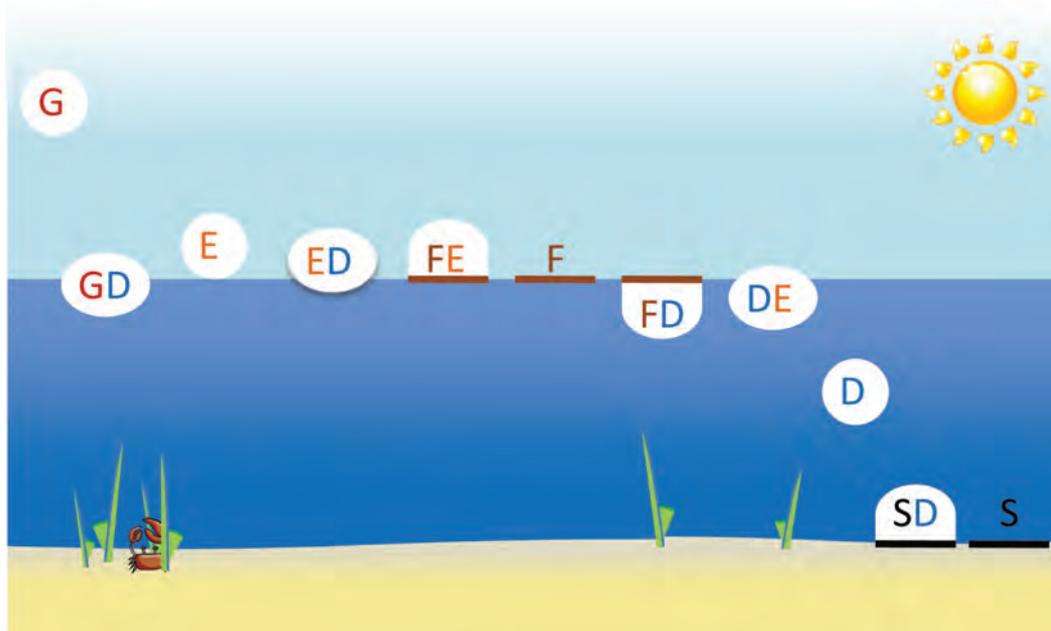
### DANGEROUS GOODS MANIFEST M/V BOXSHIP L1234567 (Inbound to Panama)

| Shipper/Consignee  | Pkg. No.       | Shipping Description   | Stowage Position | Gross Weight | Container | Port of Discharge | Shipment No. |
|--------------------|----------------|--|------------------|--------------|-----------|-------------------|--------------|
| Local Chemical Co. | 25 Drums       | ACROLEIN, class 6.1<br>UN1092, P.G. I (3),<br>Marine Pollutant                 | 030862           | 2500 Kgs     | 243917    | NYNY              | 7654321      |
| Manufacturing Co.  | 30 Tins        | ADHESIVES (liquid),<br>Class 3, UN1133, P.G. III<br>Flammable Liquid           | 420190           | 19.22 Kgs    | 678345    | NYNY              | 6453210      |
| Manufacturing Co.  | 500<br>Bottles | DICHLOROMETHANE<br>(liquid), Class 6.1,<br>UN1593, P.G. III<br>Toxic substance | 420190           | 1000 Kgs     | 678345    | NYNY              | 6465210      |

▲ Figure 4: Example of a dangerous cargo manifest, providing details of two containers containing HNS.



◀ Figure 5: The presence of an HNS can hinder the response to a spill of oil. Here unidentified bottles, covered in bunker oil, were located on the shoreline, some of which may be Aluminium Phosphide (inset) which produces highly toxic phosphine gas on contact with water. In this instance, a detailed risk assessment plan was drafted to ensure the safety of shoreline clean-up personnel (inset image courtesy United Phosphorous).



▲ Figure 6: Diagrammatic representation of the Standard European Behaviour Classification.

the properties of volatility, solubility and density and these in turn determine the hazard(s) presented by the substance (toxicity, flammability, reactivity, explosivity, corrosivity, etc).

The Standard European Behaviour Classification (SEBC) system categorises HNS into 12 groups on the basis of their dominant behaviour in water (Figure 6 and Table 3). The main properties giving indications of the behaviour of a chemical spilled at sea are listed in Table 4. However, it is important to be aware that this system only classifies chemicals according to their dominant behaviour relevant to spill response and a chemical may also exhibit other characteristics. For example, benzene is classed according to its dominant characteristic (evaporator) but it is also

|     | Property Group                | Properties                      |
|-----|-------------------------------|---------------------------------|
| G   | gas                           | evaporate immediately           |
| GD  | gas/dissolver                 | evaporate immediately, dissolve |
| E   | evaporator                    | evaporate rapidly               |
| ED  | evaporator/dissolver          | evaporate rapidly, dissolve     |
| FE  | floaters/evaporator           | float, evaporate                |
| FED | floaters/evaporator/dissolver | float, evaporate, dissolve      |
| F   | floaters                      | float                           |
| FD  | floaters/dissolver            | float, dissolve                 |
| DE  | dissolver/evaporator          | dissolve rapidly, evaporate     |
| D   | dissolver                     | dissolve rapidly                |
| SD  | sinker/dissolver              | sink, dissolve                  |
| S   | sinker                        | sink                            |

▲ Table 3: The Standard European Behaviour Classification (SEBC) System for chemicals.

soluble to a certain extent. All aspects of a substance's behaviour should be considered when planning a response.

## Hazards

Under the UN Globally Harmonized System of Classification and Labelling of Chemicals (GHS)<sup>4</sup> chemicals are classified according to the types of hazard they represent and portrayed by harmonised hazard communication with consistent labelling and Safety Data Sheets. The GHS aims to ensure that information on physical hazards and toxicity from chemicals is available to enhance the protection of human health and the environment during the handling, transport and use of these chemicals. Two sets of pictograms are included within the GHS: one for the labelling of containers and for workplace hazard warnings (Figure 7), and a second for use during the transport of dangerous goods (Figure 8).

<sup>4</sup> [www.unece.org/trans/danger/danger.html](http://www.unece.org/trans/danger/danger.html)



▲ Figure 7: GHS pictograms for HNS labelling. Left to right: flammable, explosive, oxidising, acute toxicity, corrosive, harmful/irritant, toxic to the environment, carcinogen/sensitiser and compressed gas. These are intended to replace national and regional labels.

| Property                           | Description  |
|------------------------------------|--|
| <b>Density</b>                     | Density, $\rho$ , (substance)=mass/volume. Gives an indication of the likelihood that a substance will float or sink (average density of sea water: $\rho = 1.025 \text{ g/cm}^3$ ).<br>$\rho(\text{benzene}) = 0.88 \text{ g/cm}^3$ , floats. $\rho(\text{solid phosphoric acid}) = 1.864 \text{ g/cm}^3$ , sinks.  |
| <b>Specific Gravity</b>            | Specific Gravity = $\rho(\text{substance})/\rho(\text{water})$ is a non-dimensional parameter i.e. does not have units. In fresh water also known as relative density.   |
| <b>Solubility</b>                  | The ability of a solid, liquid or gas to dissolve in a liquid (usually given for fresh water). In sea water: $s(\text{benzene}) = 0.07\%$ , slightly soluble; $s(\text{phosphoric acid}) = 100\%$ , miscible.  |
| <b>Vapour Pressure</b>             | Describes the likelihood that a substance will evaporate to form a vapour. The higher the vapour pressure, the more a substance tends to evaporate (Slow evaporator VP > 300 Pa, fast evaporator VP > 3 kPa). VP(ethylene glycol) = 500 Pa; VP(ethanol) = 5 kPa; VP(propane) = 2.2 MPa.  |
| <b>Vapour Density</b>              | Relative weight of a gas or vapour compared to air, which has an arbitrary value of one. If a gas has a vapour density of less than one it will generally rise in air. If the vapour density is greater than one, the gas will generally sink in air. The property is based on molecular weights. Molecular weight of air = 29 atomic mass units (AMU). Hydrogen = 2 AMU and thus has a vapour density of $2/29 = 0.068$ , rises. Hexane = 84 AMU: vapour density = $84/29 = 2.9$ , sinks. |
| <b>Flash Point</b>                 | The flash point of a volatile material is the lowest temperature at which it can vaporise to form a mixture in air that will ignite when exposed to an ignition source. Flash Point T(phenol) = 79°C, Flash Point T(benzene) = - 11.1°C.   |
| <b>Lower Explosive Limit (LEL)</b> | The lowest concentration (percentage) of a gas or a vapour in air capable of igniting in the presence of an ignition source. At a concentration in air below the LEL, insufficient fuel is available to burn and the air/fuel mixture is 'too lean'. Also expressed as lower flammable limit (LFL). LEL(benzene) = 1.2% by volume of air (12,000 ppm). LEL(methane ( $\text{CH}_4$ )) at 20°C = 5.1 %.   |
| <b>Upper Explosive Limit (UEL)</b> | Highest concentration (percentage) of a gas or a vapour in air capable of igniting in the presence of an ignition source. Concentrations higher than the UEL are 'too rich' to burn, also expressed as upper flammable limit (UFL). UEL(benzene) = 7.8% by volume of air (78,000 ppm).   |
| <b>Flammable Range</b>             | The concentration range between the upper and lower flammable limits.  |
| <b>Auto-ignition Temperature</b>   | Minimum temperature at which a chemical ignites when no ignition source is present. Auto-ignition T(benzene) = 538°C.  |
| <b>Boiling Point</b>               | Boiling Point T(propane) = -42°C, T(ammonia) = -33°C, T(sulphuric acid) = 337°C.   |

▲ Table 4: Key physical properties to assess the fate and behaviour of a chemical.

Either one or the other is chosen, depending on the target audience, but the two are not used together. The following hazards, as portrayed by the seven initial pictograms, may be generated by a spill of an HNS itself or by reactions between the HNS and other chemicals, water or air.

## Flammability

Flammability is the ease with which a material ignites either naturally or through the presence of an ignition source. The flammability of a liquid is governed by its vapour pressure or flash point. Flammable liquids are characterised by low boiling and flash points. Other flammable materials may catch fire spontaneously in contact with air. An HNS fire can lead to the release of heat, solid particles and toxic gases (Figure 9).

## Explosivity

An explosive substance is a chemical or mixture of chemicals that becomes unstable under certain environmental conditions, for example, by heat, friction, impact or static electricity, and releases its stored energy. Substances are classified by their sensitivity to environmental conditions, their

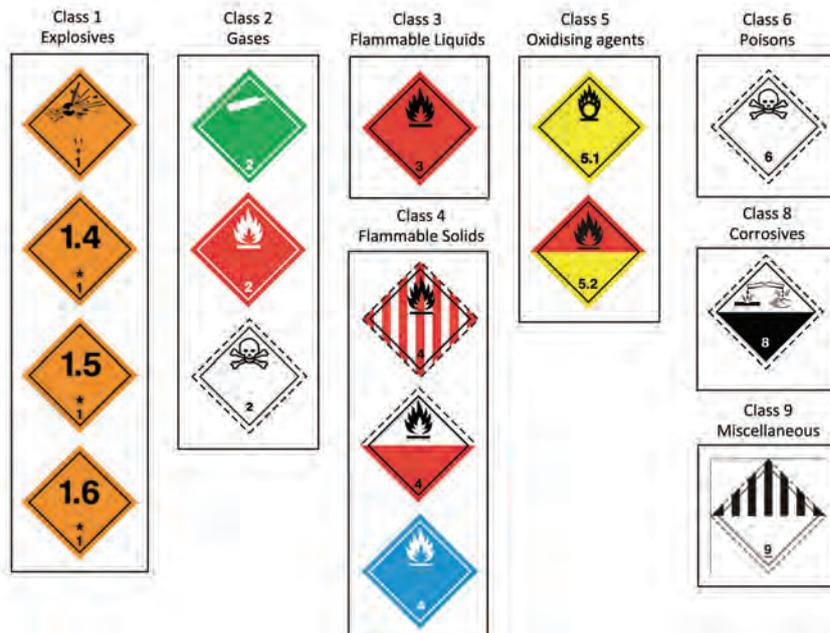
velocity upon detonation and by their chemical composition. The classification also includes such materials as pyrotechnic devices and ammunition.

Explosions can be accompanied by shockwaves, fire and heat. In particular, damage occurs when the energy released cannot be dissipated quickly. An important example of an explosive combination of a volatile material and environmental conditions is a BLEVE (Boiling Liquid Expanding Vapour Explosion); e.g. the heating of a contained, compressed, liquefied gas can lead to the rupture of the container due to overpressure following the boiling of the liquid inside. The result is an instantaneous release, that can develop into a sufficiently large flammable cloud to generate a flash fire, fireball or a vapour cloud explosion.

The lower and upper explosive limits (LEL and UEL) define the range in which a gas or a vapour in air is capable of igniting in the presence of an ignition source.

## Oxidising hazard

An oxidising hazard may be presented by substances that in



▲ Figure 8: United Nations pictograms for HNS transportation. Classes 1 to 6 and 8 are a part of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Class 7 materials (radioactive – not shown) and Class 9 (miscellaneous), while within the IMDG code symbols, are not included within the GHS.

themselves are not necessarily combustible, but by providing oxygen may cause or contribute to the combustion of other material. Strong oxidising agents, for example nitric acid ( $\text{HNO}_3$ ), can react particularly violently with organic material.

## Toxicity

Toxic chemicals include those that cause death or injury to living organisms if inhaled, ingested or absorbed through the skin at low levels. Toxicity is often measured and classified by the degree of risk a particular concentration represents to human health or the environment. Acute and chronic concentration exposure limits are often cited. Acute exposure is defined as a single exposure to a toxic substance which may result in severe biological harm or death and is usually characterised as exposure lasting no longer than a day. Chronic exposure is defined as continuous exposure to a toxin over an extended period of time, often measured in months or years, which can cause irreversible side effects. Chlorine is an example of a highly toxic gas.



▲ Figure 9: Containers collapsed and distorted by the heat of a fire on the bow section of a stranded Ro-Ro vessel.

## Corrosive hazard

Corrosive chemicals can destroy or irreversibly damage another surface or substance with which they come into contact, including both living tissues (skin, eyes, lungs) and materials such as response equipment, other cargoes or packaging. Examples include sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and sodium hydroxide ( $\text{NaOH}$ ).

## Irritant/Harmful

A chemical in this category may be harmful to health while those with irritant properties can cause inflammation to the skin (dermatitis) and mucous membranes in a live organism (for example, the eyes, throat and/or lungs).

## Environmental hazard

Chemicals that may present an immediate or delayed danger to one or more components of the environment and for which particular care should be exercised over their disposal.

## Reactivity

Chemicals may react with adjacent materials, fuel oil, water or air in a variety of ways, including corrosion, decomposition, oxidation/reduction or polymerisation reaction. It is important to know the reactivity of the substance in order to formulate an appropriate response as these reactions can generate heat and flammable or toxic gases. For example, iron may react with some strong acids or alkalis to release hydrogen that in air produces an explosive hydrogen-air mixture. Some chemicals can polymerise with the addition of heat or water. Polymerisation is often accompanied by volume expansion and the release of heat (exothermic), potentially causing damage to the container in which the material is stored. The product may also decompose into secondary products due to interactions with its surrounding environment. Particular hazards with decomposition are the formation of

gases, such as carbon dioxide (CO<sub>2</sub>) and hydrogen sulphide (H<sub>2</sub>S), that are in themselves toxic, and can result in low oxygen levels that demand safe practices for entry into ships' holds and other confined spaces. The US National Oceanic and Atmospheric Administration's (NOAA) Office of Response and Restoration<sup>5</sup> provides a downloadable Chemical Reactivity Worksheet (CRW) that allows the user to determine the reactivity of a substance with air, water and other chemicals.

## Hazard assessment

When ranking the hazards presented by the loss of a particular cargo, two easily accessible and simple guides provide an important first step in evaluating the potential severity of an incident: Annexes II and III of MARPOL 73/78 and the GESAMP hazard profiles.

### The MARPOL Convention

The MARPOL Convention is the primary international convention covering prevention of pollution from ships. Two annexes of MARPOL are relevant to HNS:

#### Annex II

MARPOL Annex II contains regulations for bulk liquid cargoes that may cause environmental pollution if discharged at sea. Within the Annex, four categories are defined according to the hazard that the bulk liquid presents to human health, marine resources and amenities. Appendix II of Annex II contains a list of substances grouped according to the four categories shown below:

- **Category X** – liquid substances that are deemed to present a major hazard to either marine resources or human health and therefore justify the prohibition of the discharge into the marine environment;
- **Category Y** – liquid substances that are deemed to present a hazard to either marine resources or human health or cause harm to amenities or other uses of the sea and therefore justify a limitation on the quality and quantity of the discharge into the marine environment;
- **Category Z** – liquid substances that are deemed to present a minor hazard to either marine resources or human health and therefore justify less stringent restrictions on the quality and quantity of the discharge into the marine environment; and
- **Category OS** – these 'other substances' are deemed to fall outside of categories X, Y, and Z and are deemed to present no harm to marine resources, human health, amenities or other uses of the marine environment.

#### Annex III

Annex III deals with the provisions for the prevention of pollution by harmful substances carried by sea in packaged form. As part of these regulations, any substances that are environmentally harmful (known as marine pollutants) must

be clearly marked and labelled as a 'marine pollutant' to distinguish them from less harmful cargoes (*Figure 10*).

### GESAMP hazard profiles

The hazards presented by HNS to both humans and the marine environment have been summarised by the Group of Experts on Scientific Aspects of Marine Environmental Protection (GESAMP), an advisory body to the United Nations established in 1969. The Group comprises individual experts in their field drawn from a wide range of relevant disciplines.

GESAMP has published a Hazard Evaluation of Substances Transported by Ships<sup>6</sup> that addresses the hazards presented by the most commonly transported chemicals that enter the marine environment through operational discharge, accidental spillage or loss overboard from ships. The properties of each chemical have been evaluated in relation to a number of predefined effects should any of the listed chemicals be spilled at sea. This information is collated into a hazard profile that identifies the hazardous characteristics for each substance according to the following categories:

- a. Bioaccumulation and biodegradation;
- b. Aquatic toxicity;
- c. Acute mammalian toxicity;
- d. Irritation, corrosion and long term health effects; or
- e. Interference with other uses of the sea.

Hazard profiling by GESAMP is an ongoing process and an updated listing is maintained by the IMO<sup>7</sup>.

### Human health concerns

Besides the effects associated with hazards such as the shock wave of an explosion, fire injuries or oxygen depletion, exposure to chemical substances may also occur as a result of absorption via contact with the skin, inhalation or ingestion. Inhalation is a major route of entry for gases and particles. Absorption can occur through a healthy skin, or through the chemically damaged surface of the skin (for example burns or dermatitis). Ingestion occurs when a hazardous agent is swallowed.

HNS manufacturers and others publish Material Safety Data Sheets (MSDS) that summarise the specific hazards associated with each substance. Over time these will be replaced by Safety Data Sheets (SDS) under the UN GHS. MSDS and SDS both broadly follow the same format (*Figure 11*) and provide the information contained in Table 5. Nevertheless, it should be noted that, in terms of reliability and comprehensiveness, the quality of the information currently provided by MSDS can vary considerably between



◀ *Figure 10: Marine pollutant placard. This placard does not relate to a specific class of hazard and is used when shipping any marine pollutant.*

<sup>5</sup> <http://response.restoration.noaa.gov>

<sup>6</sup> [www.gesamp.org/publications/publicationdisplaypages/rs64](http://www.gesamp.org/publications/publicationdisplaypages/rs64)

<sup>7</sup> [www.imo.org/OurWork/Environment/PollutionPrevention](http://www.imo.org/OurWork/Environment/PollutionPrevention)

|  |
|--|
| 1. Identification                        |
| 2. Hazard(s) identification              |
| 3. Composition/ingredients               |
| 4. First-aid measures                    |
| 5. Fire-fighting measures                |
| 6. Accidental release measures           |
| 7. Handling & storage                    |
| 8. Exposure controls/personal protection |
| 9. Physical & chemical properties        |
| 10. Stability & reactivity               |
| 11. Toxicological information            |
| 12. Ecological information               |
| 13. Disposal considerations              |
| 14. Transport information                |
| 15. Regulatory information               |
| 16. Other information                    |

▲ *Table 5: Information provided by MSDS and SDS.*

different providers and it is important to make every attempt to obtain information from the manufacturer of the specific cargo involved in an incident. It is anticipated that with the full implementation of GHS, Safety Data Sheets will provide more consistent and reliable information.

## Exposure limits

The chemical industry and specialised government agencies have established exposure limits to protect workers dealing with hazardous substances. Permissible exposure limits (PEL) are regulatory limits on the maximum amount or concentration of a substance in the air. A PEL is established using a time-weighted average (TWA) exposure, usually eight hours (a typical work day). These limits are based on Threshold Limit Values (TLV) that reflect the exposure to airborne gases and vapours that a typical worker can experience without serious risk of disease or injury. These limits are intended to allow for chronic exposure to hazardous substances but are not intended to deal with acute exposures following a spillage.

In order to deal with immediate effects, short-term exposure limits and ceiling limits have sometimes been established. The short-term exposure limit is one that addresses exposure to a maximum concentration over a 15 minute period and cannot be repeated more than four times a day. A ceiling limit is one that may not be exceeded for any period of time and is applied to irritants and other materials that have immediate effects. In this respect, the criterion, Immediately

**SIGMA-ALDRICH** SAFETY DATA SHEET  
 according to Regulation (EC) No. 1907/2006  
 Version 4.2 Revision Date 03.12.2011  
 Print Date 01.02.2012

**1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING**

**1.1 Product Identifiers**  
 Product name: Dichloromethane  
 Product Number: 270997  
 Brand: Sigma-Aldrich  
 Index-No.: 802-004-00-3  
 CAS-No.: 75-09-2

**1.2 Relevant identified uses of the substance or mixture and uses advised against**  
 Identified uses: Laboratory chemicals, Manufacture of substances

**1.3 Details of the supplier of the safety data sheet**  
 Company: Sigma-Aldrich Company Ltd.  
 The Old Brickyard  
 NEW ROAD, GILLINGHAM  
 Dorset  
 SP8 4XT  
 UNITED KINGDOM  
 Telephone: +44 (0)1747 833000  
 Fax: +44 (0)1747 833113  
 E-mail address: eurtechserv@sial.com

**1.4 Emergency telephone number**  
 Emergency Phone #: +44 (0)1747 833100

**2. HAZARDS IDENTIFICATION**

**2.1 Classification of the substance or mixture**  
 Classification according to Regulation (EC) No 1272/2008 [EU-GHS/CLP]  
 Carcinogenicity (Category 2)  
 Classification according to EU Directives 67/548/EEC or 1999/45/EC  
 Limited evidence of a carcinogenic effect.

**2.2 Label elements**  
 Labelling according Regulation (EC) No 1272/2008 [CLP]  
 Pictogram:

Signal word: Warning  
 Hazard statement(s): H351 Suspected of causing cancer.  
 Precautionary statement(s): P261 Use personal protective equipment as required.  
 Supplemental Hazard Statements: none  
 According to European Directive 67/548/EEC as amended.  
 Hazard symbol(s):

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▲ *Figure 11: Example of the first page of a manufacturer's SDS for dichloromethane.*

Dangerous to Life or Health (IDLH), is the ceiling exposure limit most frequently used and describes an atmosphere that is immediately dangerous to life or health for a typical adult male. IDLH limits were originally created to assist in making decisions regarding respirator use. Two factors are considered when defining IDLH limits: workers must be able to escape the hazardous environment and should not suffer permanent health damage or severe eye or respiratory tract irritation or other conditions that might impair their escape.

More specific guidelines for responding to potential releases of airborne substances continue to be developed by the industry and by government agencies, for example the US Environmental Protection Agency<sup>8</sup>.

**ERPG** (Emergency Response Planning Guidelines) are air concentration guidelines for single exposures to hazardous substances and are intended for use as tools to assess the adequacy of accident prevention and emergency response plans. ERPG are developed by the ERPG Committee of the American Industrial Hygiene Association (AIHA)<sup>9</sup>.

**AEGL** (Acute Exposure Guideline Levels) are intended to describe the risk to humans resulting from once-in-a-lifetime, or rare, exposure to airborne chemicals. The development of AEGL is a collaborative effort of the public and private sectors worldwide. The US National Advisory Committee for

<sup>8</sup> [www.epa.gov/osweroe1/docs/chem/tech.pdf](http://www.epa.gov/osweroe1/docs/chem/tech.pdf)

<sup>9</sup> [www.aiha.org](http://www.aiha.org)

the Development of Acute Exposure Guideline Levels for Hazardous Substances (AEGLC Committee)<sup>10</sup> is involved in developing these guidelines to help deal with emergencies involving spills or other catastrophic exposures.

**TEEL** (Temporary Emergency Exposure Limits) are levels of concern representing the adverse health effects of a hazardous substance on the general public. TEEL are defined by the U.S. Department of Energy<sup>11</sup> for use when ERPG or AEGLC are not available.

## Effects on marine resources

The effects of one or more chemicals on the marine environment depend on a number of factors. Most significant is the toxicity of the chemicals or mixture of substances lost or their reaction products. The extent of the impact will also depend on the quantities involved and resulting concentrations in the water column, as well as the length of time that biota are exposed to that concentration and the sensitivity of the organisms to the particular chemical or chemicals. Not only do different aquatic species exhibit different tolerances to substances, but the tolerance of a given species can vary according to different stages in its life cycle and the season. The prevailing meteorological conditions and local topography can also strongly influence the effects of a spill. In calm conditions, the area exposed to adverse effects may be relatively small and expand only slowly, with the intensity of impact diminishing with distance from the spill source. On the other hand, in a river or confined waterway, a moving plume can travel downstream quickly, exposing a rapidly expanding area to high or damaging concentrations.

In the open sea, tidal ebb and flow, ocean currents and turbulent diffusion usually result in the rapid dilution of pollutants. However, even if concentrations are below levels that would result in mortality, sub-lethal concentrations can nevertheless lead to other effects. Chemically-induced stress can reduce the overall ability of the organism to reproduce, grow, feed or otherwise function normally. Also of importance is the potential of chemicals, even at these sub-lethal levels, to disrupt other legitimate uses of the sea, for example, through tainting of fish or closure of beaches.

Some substances can persist for long periods in the marine environment once lost into the sea, including elements such as mercury and other heavy metals and some organic compounds, such as pesticides, that do not break down easily. The uptake of such substances by living organisms can lead to their 'bio-accumulation'. Bio-accumulation refers to the build up of the persistent material within an organism, and in particular within certain tissues, at a rate exceeding the rate of elimination by metabolic breakdown or excretion. Sessile marine organisms that filter seawater for food, such as bivalve molluscs (oysters and mussels), are particularly vulnerable to exposure. 'Bio-magnification', the sequential increase in concentration of a bio-accumulative substance

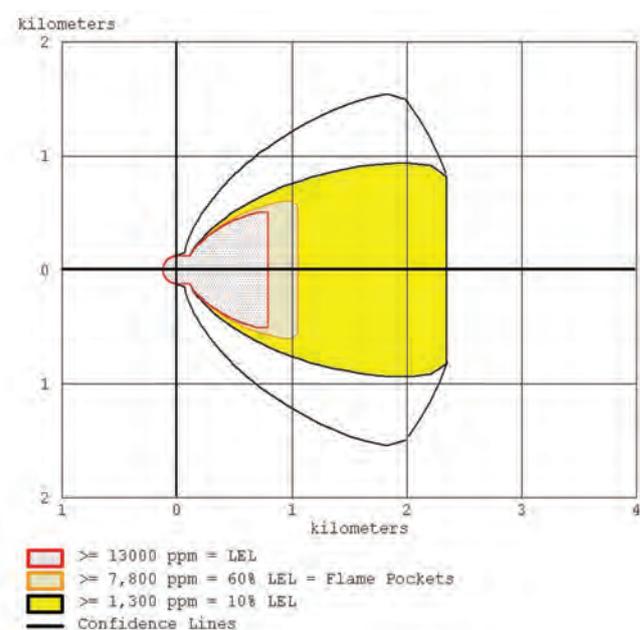
from prey to predator, may also occur up the food chain. Consequently, the highest concentrations of the substance are typically found within the tissues of the top predators, for example, increasing from minute quantities in plankton to higher concentrations in fish and eventually resulting in significant body burdens in humans.

## Planning a response to an HNS incident

The potential consequences of a spill involving HNS on human health are such that effective organisation and planning of a response is crucial. The role of each member of the response team should be defined clearly and their responsibilities and capabilities identified. Training and exercise requirements should be detailed in a contingency plan and put into effect in order to provide response personnel with the skills necessary to do their jobs safely.

### Risk assessment

When responding to accidents involving HNS, the first steps to be taken are much the same regardless of the substances involved, the circumstances of the incident and its location. It is essential not to respond on-site to a chemical incident until a thorough assessment of the situation has been carried out, focusing in particular on the health and safety aspects. It is important to identify all the chemicals involved, noting their mode of transport (bulk, container, palletted goods, drums, etc.) as well as the nature of the spill or discharge (e.g. escaped chemicals, lost packaged dangerous goods). The risk of fire and explosion, as well as health risks and risks to adjacent areas must be assessed quickly and information from sources, such as the Emergency Response Guidelines (ERG) of the IMDG Code, individual MSDS, International Chemical Safety Cards (ICSC)<sup>12</sup> and chemical information databases, for example NOAA's CAMEO<sup>13</sup>, can be helpful.



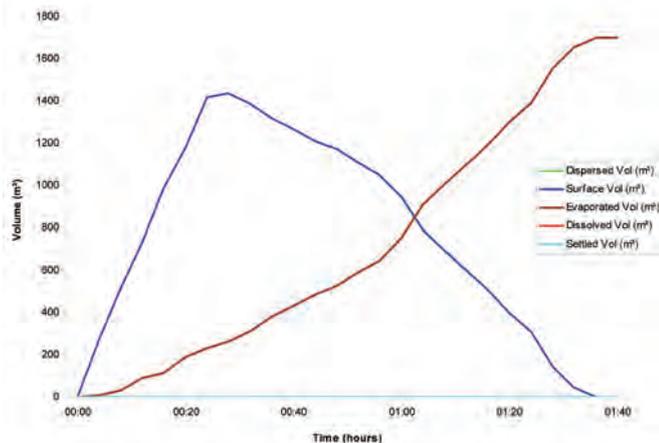
▲ Figure 12: Example of the output of the ALOHA model (NOAA) showing various levels of concern (explosivity) for cyclohexane in relation to the distance from the source. ALOHA = Area Locations of Hazardous Atmospheres.

<sup>10</sup> [www.epa.gov/opptintr/aegl](http://www.epa.gov/opptintr/aegl)

<sup>11</sup> [www.hss.doe.gov](http://www.hss.doe.gov)

<sup>12</sup> [www.ilo.org/icsc](http://www.ilo.org/icsc)

<sup>13</sup> Computer Aided Management of Emergency Operations



◀ *Figure 13: Example of the modelled behaviour of a finite volume of cyclohexane ( $C_6H_{12}$ ) over time, as released from a sunken wreck. The graph indicates cyclohexane would rise to the water surface and steadily evaporate to the atmosphere. The maximum surface slick area would be reached 20 hours after the initial release. As cyclohexane is immiscible and has a density of  $0.78\text{ g/cm}^3$ , the dissolved and settled (i.e. sunk to the sea floor) volumes, as well as the dispersed volume, are negligible or zero (Source: Chemsys – National Chemical Emergency Centre (NCEC), <http://the-ncec.com>).*

Based on the physical properties of the chemicals as well as environmental conditions (such as air and water temperature, water movement and the prevailing wind strength and direction) a relatively simple, first estimate of the probable fate and behaviour of the chemical can be made. Only after these hazards have been identified and any risk of further leakage established, can an initial risk assessment be completed and an appropriate response strategy considered.

## Modelling

A number of different computer models exist, some of which provide predictions on the likely spread of chemicals (Figures 12 and 13) in two dimensions, for example, across the water surface, while others consider dispersion in three dimensions in air and in the water column. However, computer models have a number of limitations, including the general

assumptions made to develop the model's algorithms and source code, and very few have been validated against actual spills. In addition, factors such as the reliability of input data and the operator's level of training and skills of interpretation also need to be taken into account when reviewing the model output. Nevertheless, they provide a useful tool for contingency planning and, to a limited extent, in response operations, especially when combined with real-time monitoring and particularly when the HNS is colourless.

## Monitoring

Monitoring forms a crucial part of the response to a chemical spill and for gases and substances that rapidly evaporate, it may be the only form of response. Two forms of monitoring may be conducted during the response phase: air dispersion monitoring and monitoring the spread of chemicals in water

| Detector   | Detection method   | Advantages  | Disadvantages  |
|--|--|---|--|
| <b>Chemical detection paper</b>                      | Changes colour upon exposure to an HNS, according to the type of HNS.  | One of the least sophisticated and least expensive methods.   | Lacks specificity and is prone to false-positive readings.   |
| <b>Colorimetric tubes e.g. Draeger and RAE tubes</b> | A gas sample is drawn into a specific tube, allowing the concentration to be read. 160 substance-specific reagent tubes are available to identify different HNS.                             | Simple and inexpensive way of detecting and identifying an HNS.   | A different tube must be used for each HNS. Knowledge of the likely HNS present is required to prevent false negatives. One-off use. |
| <b>Photo-ionisation Detector (PID)</b>               | Suspect gas is ionised by ultraviolet light with specific ranges of UV ionising molecules in certain HNS. An ion detector registers the ionised molecules.                                   | Highly sensitive. Relatively inexpensive. Can produce instantaneous readings and operate continuously.  | The user must know with high certainty the identity of the gas or vapour to be detected.   |
| <b>Ion mobility spectroscopy (IMS)</b>               | A gaseous sample is ionised by radioactive emitters and compared to a sample of clean air. An HNS, identified according to pre-determined parameters, causes an alarm to sound.              | It is less sensitive to contaminants because it relies on a clean air sample for calibration. Instantaneous readings. Many commercial variants available. | Relatively expensive. Generally limited to military or industrial use.   |
| <b>Infrared spectroscopy</b>                         | Mid-IR light (frequency $4000\text{ cm}^{-1}$ to $200\text{ cm}^{-1}$ ) is used to excite gaseous molecules. Each gas has a unique infrared fingerprint. Detection causes an alarm to sound. | Highly selective technique. Various detector types available – hand-held or remote stand-alone devices.   | Relatively expensive.  |

▲ *Table 6: Advantages and disadvantages of a number of HNS detector types available for real-time monitoring.*

(on the surface, in the water column or on the seabed). Monitoring is carried out for a number of purposes:

- to identify the specific chemicals spilled;
- to detect the presence or absence of substances;
- to measure the concentration of substances;
- to establish a safety perimeter; and
- to validate models.

## Air monitoring

Real-time monitoring can be used to assess toxic, fire and explosion hazards, to help determine safe working areas or potential evacuation zones and to assist with decisions on the appropriate level of personal protective equipment (PPE). For example, monitoring using chemical cell oxygen meters can be carried out to check for oxygen deficient environments and, if the atmosphere is found to contain less than 19.5% oxygen, Self-Contained Breathing Apparatus (SCBA) should be worn.

Equipment of varying degrees of sophistication is available for monitoring HNS (*Table 6*). One of the key factors to be taken into account when selecting equipment is how quickly results will be obtained as, to be of most use, information needs to be in 'real time'. A further important consideration is whether the monitoring equipment is autonomous and can be deployed remotely. If it requires human intervention, for example a hand-held device (*Figure 14*), then clearly operators must be properly protected with the appropriate PPE. It is also necessary to recognise that all equipment will require training in its use and some designs will require calibration.

## Water monitoring

Some analysis techniques may be useful for determining the concentrations of HNS in the water column. Some organic substances can be monitored using, for example, portable gas chromatography (GC), Mass Spectroscopy linked to Gas Chromatography (portable GCMS), titration methods or ultra violet (UV) / infra red (IR) spectroscopy. Sensor based probes are available for the measurement of inorganic parameters such as biological oxygen demand (BOD), turbidity, conductivity, pH, ammonium ions, bromide, chlorine and copper, while simple



▲ *Figure 14: Demonstration of a hand-held phosphine gas monitor outside a hazardous area.*

methods such as indicator papers can be used to indicate acidity and alkalinity. In other cases, biological impacts such as bleaching or mortality of marine organisms may make it possible to track the dispersion of a pollutant. Sinking chemicals are more difficult to monitor but the use of sonar, underwater video cameras mounted on a Remotely Operated Vehicle (ROV) or a matrix of weighted sorbents may allow the spread of the pollutant to be mapped on the sea bed.

## Personal Protective Equipment (PPE)

Following an initial risk assessment, an evaluation team is usually mobilised to the vicinity of the casualty to assess the situation and to determine whether any mitigating actions are possible on the vessel. Clearly, it is essential that the evaluation team and responders wear the correct PPE.

PPE refers to the clothing and respiratory equipment necessary to protect a person from the hazardous properties of chemicals. Its selection should be appropriate to the particular hazards associated with the chemicals spill. Unfortunately, no single material can be used to protect against all chemicals as the ability of the material to perform as a barrier depends on how long the material is exposed to the chemical, the concentration of the chemical and the external temperature. If the chemical that was spilled has not been identified, responders should assume a worst case scenario and wear the highest level of protection. As more information becomes available, an informed decision can be made as to whether it is appropriate to downgrade the level of PPE. As well as the resistance of the PPE material to the chemicals spilled, other factors to take into consideration when choosing appropriate PPE include the level of respiratory protection required, the durability of the PPE material and the effect that the PPE may have on heat stress and the responder's ability to undertake specific work tasks.

A number of government agencies, including the US Occupational Safety and Health Administration (OSHA)<sup>14</sup> has devised four categories of PPE based on the level of protection afforded (Levels A, B, C and D). These four levels are recognised by most response organisations. Level A offers the highest level of protection (*Figure 15*), whereas Level D protection could be considered as a work uniform, and should only be worn when it is certain that personnel will not be exposed to harmful levels of HNS. *Table 7* shows the constituent items of PPE for each of the levels A to D, although additional items such as hard hats and safety glasses may also be included within each level. It is important that responders are thoroughly trained in the use of PPE to minimise the risk of harm through the use of the PPE itself or through their use in the wrong circumstances.

## Response options for HNS spills

The response to a spill should be proportional to the threat posed by the volume and hazards presented by the particular chemicals lost to the sea. The volume and containment of

<sup>14</sup> [www.osha.gov](http://www.osha.gov)

| Personal Protective Equipment (PPE)                    | Level A | Level B | Level C | Level D |
|--|---------|---------|---------|---------|
| Self Contained Breathing Apparatus (SCBA)              | x       | x       |         |         |
| Full face or half mask respirator                      |         |         | x       |         |
| Totally Encapsulating Chemical Protection Suit (TECPS) | x       |         |         |         |
| Hooded, chemical resistant clothing                    |         | x       | x       |         |
| Chemical resistant outer gloves                        | x       | x       | x       |         |
| Chemical resistant inner gloves                        | x       | x       | x       |         |
| Chemical resistant boots                               | x       | x       |         |         |
| Disposable protective suit                             | x       |         |         |         |
| Coveralls  |         |         |         | x       |

▲ Table 7: Items of equipment required for each level of protection according to the US OSHA.

a product will affect the response; for example, the release of an entire tank of acid from a chemical tanker may have a much more rapid and damaging effect than a damaged container, in which a small number of bottles of acid are ruptured. Also, some chemicals such as aluminium and cyanides become far more toxic in acidic conditions (low pH) and consideration must be given to secondary reactions with other substances that they may come into contact with and hazards that may result. In every instance, responders must wear the appropriate PPE and response and monitoring equipment must be adequately designed to enter hazardous atmospheres, for example with suitable air filtering equipment or spark-proof engines.

The following provides a brief summary of potential response techniques for the different groups of chemicals.

## Gases & evaporators

The release of a gas or evaporating liquid HNS has the potential to generate vapour clouds that might be toxic or form an explosive mixture with air. As a result, there may be potential health and safety implications for the crew of the casualty, responders and centres of population nearby. When such incidents occur near centres of population, the local fire service often have the commanding role in the response.



▲ Figure 15: Responders equipped with Level A Personal Protective Equipment.

In order to plan a response, it is important to know how the gas or vapour will behave and the likely trajectory of the hazardous cloud. Computer modelling of the airborne contaminants is likely to assist in forecasting the movement, spread and fate of the plume as it disperses. Safety zones can then be put into place as necessary and the public advised as appropriate.

It may be an option to manoeuvre the casualty so that toxic, corrosive or flammable vapours are carried away from populated areas. If this is not possible, the authorities may need to advise the public to remain indoors and to close doors and windows or, in severe cases, the order may be given to evacuate locations under threat. Evacuation brings with it associated risks, for example of panic, particularly in large population centres and these have to be balanced against the potential consequences if the population remains in place.

Response techniques such as ‘knocking down’ a vapour cloud, or attempting to stop or deflect it using water sprays or foam, are measures that may be available to responders who should, however, be aware of the possible reactions with water and balance any consequences against the risks. Consideration should also be given to the consequences of generating large volumes of contaminated water and the



▲ Figure 16: An exercise simulating a response to a spill of HNS using fire vessels (image source unknown).



▲ *Figure 17: Plume of rock phosphate escaping from a casualty.*

stability of the casualty in case of flooding. These methods can be used with any water soluble gases, such as ammonia and sulphur dioxide. The risk of fire and explosion of non-water soluble gases can be reduced by cooling hot surfaces and suppressing sparks and flames (*Figure 16*) using water spray and foam.

In an open environment, toxic vapour will usually disperse as a result of natural air movement and turbulence. Often the only feasible response measure will be to monitor the cloud and its dispersion.

## Dissolvers

A significant proportion of the chemicals transported by sea are soluble substances. A dissolving chemical lost to the sea will form a growing 'plume' of decreasing concentration as the plume moves away from the source (*Figure 17*). Many dissolvers are not visible and rapidly disperse, meaning that monitoring concentrations in the water column may not be straightforward. However, computer models can give useful indications of the likely distribution and fate of the substance and predict potential hazards to the marine environment and other resources such as fisheries, water intakes and recreational areas. Where elevated concentrations are anticipated, monitoring will be essential to verify the computer generated predictions.

The ability to contain and recover dissolved chemicals is extremely limited. Providing means to accelerate the natural processes of dispersion and dilution may be the only way to respond to such chemicals. Some dissolved chemical plumes may, in theory, be neutralised, flocculated, oxidised or reduced by the application of other chemicals. On land and in confined water bodies, and with the approval of the relevant authorities, neutralising agents may be effective tools if applied correctly. Products that could be used for treatment of chemicals in water, such as flocculation agents, gelling agents, activated carbon, complexing agents (chemicals that trap contaminants within their molecular structure) and ion exchangers, should have the following attributes:

- be non toxic;
- the neutralising process and by-products must be non toxic;

- have low biological oxygen demand (BOD);
- be safe to use by trained personnel;
- be easy to handle and store; and
- be commonly available at a reasonable cost.

Nevertheless, in the open sea, the time delay between a spill and the response, together with the large volume of water involved, invariably mean that chemical treatment is unlikely to be practical or provide any benefit and would not normally be recommended.

## Floaters

Floating chemicals can be low or high viscosity liquids, or may even be solid. If the spilt chemical has a high vapour pressure it may evaporate quickly and form a vapour cloud above the slick. Many floaters will spread across the water surface to form a slick in a similar manner to oil. However, unlike oil they may not be visible on the water. For spills involving relatively persistent chemicals that float, it may be possible, in some cases, to detect and monitor floating materials using technologies such as aerial surveillance (SLAR, IR and UV) and possibly satellite imagery, although there is limited practical experience of using these techniques for HNS spills.

If safe, it may be possible to consider deploying booms to contain and control the movement of substances on the water's surface. Skimmers and other oil spill response equipment may also be used to recover the material from the surface of the water. However, prior to use, it is important to ensure that the spilt chemical will not react adversely with the equipment or explode if a spark is generated. Containment and recovery may not be advisable when dealing with highly toxic or flammable HNS as containment could lead to increased concentrations creating very dangerous environments for responders and the local population. In such cases it is often preferable to allow natural dissipation to reduce the concentrations to below harmful levels. Where fire and explosion is a risk and legislation allows, emergency responders may apply fire-fighting or suppressant foams.

In certain circumstances, sorbent materials may be deployed to collect and concentrate an HNS spill. An important distinction should be made between absorbents that incorporate the spilt chemical into the structure of the material and adsorbents whereby the chemical coats the surface of the sorbent material. Absorbents encapsulate a spilt chemical, preventing its release and reducing its volatility. Conversely, the use of adsorbents can increase the surface area of the spilt chemical with an attendant increase in the rate of vapour release. Furthermore, an adsorbent may exhibit poor retention of the recovered chemical as the material is recovered from the water. Although used extensively on land based spills, the deployment and recovery of sorbents in a marine environment is less effective. The use of sorbent booms or mats is preferred over loose powders or fibres as collection of the latter is often unachievable. The main disadvantages of sorbent products are that they can be expensive and they produce a higher volume of contaminated material that is bulky to transport and must be disposed of in compliance with local regulations.

In some cases, it may be possible to burn-off a floating chemical, but due consideration must be given to the possibility of the formation of toxic fumes leading to health and safety concerns for responders and the uncontrolled spread of the fire and smoke.

## Sinkers

Chemicals that sink have the potential to contaminate the seabed and may sometimes persist in the sediment. The response to sunken chemicals may therefore need to consider the recovery of the chemical and any heavily contaminated sediment. In shallow waters, mechanical dredgers and pump/vacuum devices may be used to recover sunken substances. Careful attention will also need to be given to the treatment and disposal of recovered chemicals and contaminated sediments.

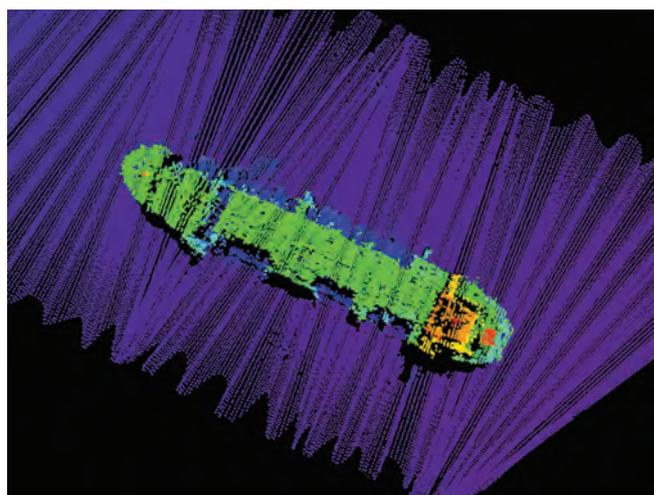
## Sunken wrecks

HNS cargo remaining within a sunken wreck (*Figure 18*) is likely to raise concerns with respect to the potential risk associated with its future release, either sudden and catastrophic or continuous over a long time period. In such cases, a risk assessment should be undertaken to determine which of the following three main approaches usually considered by responders, should be followed:

- **Passive release** through vents and/or following the long term corrosion of the vessel's hull. This approach is adopted when the risk assessment shows that a release is unlikely to result in significant damage to the environment

or when no other option is feasible.

- **Controlled release** of the cargo is usually considered for substances, e.g. dissolvers, which may result in some localised impacts, but which are unlikely to cause widespread damage if released relatively slowly into the water column, although a sudden release could cause concern.
- **Cargo removal** is considered for substances raising the highest levels of concern in terms of potential damage to human health, the environment and economic activities in the vicinity.



▲ *Figure 18: Sonar imagery of the wreck of a sunken chemical tanker (image courtesy NOAA).*

## Key points

- If a chemical is flammable, explosive, an oxidising agent, corrosive, an irritant or an environmental hazard, it is likely to be considered a Hazardous and Noxious Substance (HNS).
- The physical properties of HNS govern their behaviour when lost into the sea and determine whether the substance behaves as a gas, evaporates, dissolves or sinks.
- The effects of an HNS on the marine environment depends on the toxicity, exposure and sensitivity of marine organisms to the chemical concerned.
- It is important to anticipate the potential reaction of certain HNS with water, on exposure to air, or if several chemicals are spilt, with each other to produce heat or toxic products.
- Hazards to human health and the marine environment have been evaluated by GESAMP while exposure limits for humans are expressed as IDLH, ERPG, AEGL and TEEL to assist with the safe response to HNS incidents. Relevant data is provided in Safety Data Sheets.
- Before responding to an HNS incident, it is essential that a risk assessment is conducted based on modelling and monitoring of HNS pollutant levels.
- Response options depend largely upon whether the substance is a gas, evaporator, dissolver or sinker. For gases and substances that evaporate or dissolve quickly, monitoring may be the only form of response while recovery may be possible for some floaters and sinkers.
- Four levels of PPE are widely recognised, A, B, C and D, with A offering the highest level of protection. PPE appropriate to the hazard should be selected but when high levels of protection are required it is vital to take environmental conditions into account when setting the length of work periods.

## TECHNICAL INFORMATION PAPERS

- 1 Aerial Observation of Marine Oil Spills
- 2 Fate of Marine Oil Spills
- 3 Use of Booms in Oil Pollution Response
- 4 Use of Dispersants to Treat Oil Spills
- 5 Use of Skimmers in Oil Pollution Response
- 6 Recognition of Oil on Shorelines
- 7 Clean-up of Oil from Shorelines
- 8 Use of Sorbent Materials in Oil Spill Response
- 9 Disposal of Oil and Debris
- 10 Leadership, Command & Management of Oil Spills
- 11 Effects of Oil Pollution on Fisheries and Mariculture
- 12 Effects of Oil Pollution on Social and Economic Activities
- 13 Effects of Oil Pollution on the Environment
- 14 Sampling and Monitoring of Marine Oil Spills
- 15 Preparation and Submission of Claims from Oil Pollution
- 16 Contingency Planning for Marine Oil Spills
- 17 Response to Marine Chemical Incidents

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