2.8 HAZARDOUS MATERIALS

2.8.1 Hazardous material spills

This chapter of the Counter Pollution Manual deals with incidents involving Hazardous and Noxious Substances (HNS). It contains brief information for Operational Control Authorities (OCA) and On-Scene Co-ordinators (OSC) about the procedures to be followed, and possible measures to be taken, after notification has been received that an accidental spillage of bulk “chemicals” or packaged goods containing hazardous substances other than oil has occurred.

In this chapter, categories of chemical substances (based on their physico-chemical characteristics) are described according to their behaviour, together with the risks posed to human health and the environment so that the appropriate techniques for responding to the spill, and measuring and detecting the spill, can be selected.

The procedure that should be followed to assess the risks posed by a chemical spill and to decide on the most appropriate way to respond is outlined in the following flow diagram:

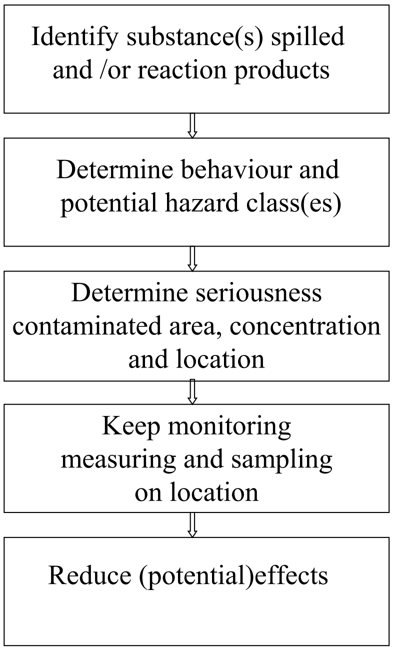

Figure 2.8.1 Flow diagram of general approach to a chemical spill

Once the hazardous substance that has been released has been identified (Name, UN number, CAS number and/or IMDG class) an assessment of the potential risks can be made. If there is a reaction with water or air the reaction products also need to be taken into account.

Based on the state of aggregation, the density, solubility and vapour pressure, the behaviour class can be identified (see Figure 2.8.3). Once the behaviour class is known the potential hazards can be identified (see Figure 2.8.4).

For decision making purposes it is important to determine first the seriousness of the spill situation. Computer models in combination with on scene measurements and/or sampling can be used for this purpose. In sections 2.8.3 and 2.8.4 rules of thumb and back of envelope calculations are given to determine an estimation of the contaminated area. By defining the seriousness of the situation, an informed decision can be made about the most appropriate way of responding to the situation. Use of the classification systems described in section 2.8.2

is a fast and relatively simple way to select the most appropriate response action from those described in section 2.8.7.

2.8.2 Categorisation of hazardous substances

Thousands of different chemical substances are transported by sea in bulk or in packaged form. Modern chemical tankers vary in size from 1 000 to 50 000 ton dead weight. Most tankers used to transport chemicals and dangerous goods are double hulled, in order to prevent the release of cargo in the event of a collision or grounding. A large tanker can contain up to 35 different tanks each containing a different chemical. Chemical tankers have to abide by specific regulations controlling the storage of substances. Packaged goods are often transported in containers with numerous different substances on board of one vessel. Less dangerous liquid cargoes are transported in single hull vessels.

The probability of an accident is limited but always present as recent ship incidents involving chemicals have shown. Dealing with individual chemicals during a chemical spill is complex and requires chemical expertise. Chemical substances have therefore been grouped in behaviour categories and hazard effect categories to facilitate decision making in the case of a chemical spill. This is in order to limit the number of standard response approaches to chemical spills. The choice of the appropriate approach is based on (1) short term behaviour of a spill released into the water and (2) the potential hazards of a possible release.

When gases, liquids or solids enter the marine environment various types of behaviour are possible. This depends on the solubility, density and vapour pressure of the substance involved.

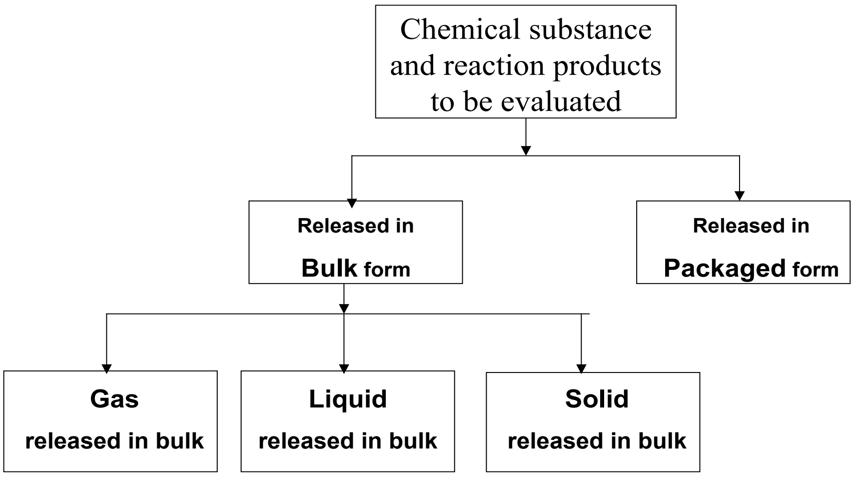

Figure 2.8.2 Primary release forms of chemical substances spilled in the marine environment

Released substances can form gas clouds, evaporate from the water surface, float on the water surface, dissolve into the water column, sink to the bottom, or show combinations of these behaviour types. Physico-chemical properties such as solubility, density and vapour pressure mainly determine the short-term behaviour of the substances in the marine environment. Based on the short-term behaviour which is most relevant for response actions, released chemical substances can be divided into four major behaviour categories and ten sub-behaviour categories (see Figure 2.8.3).

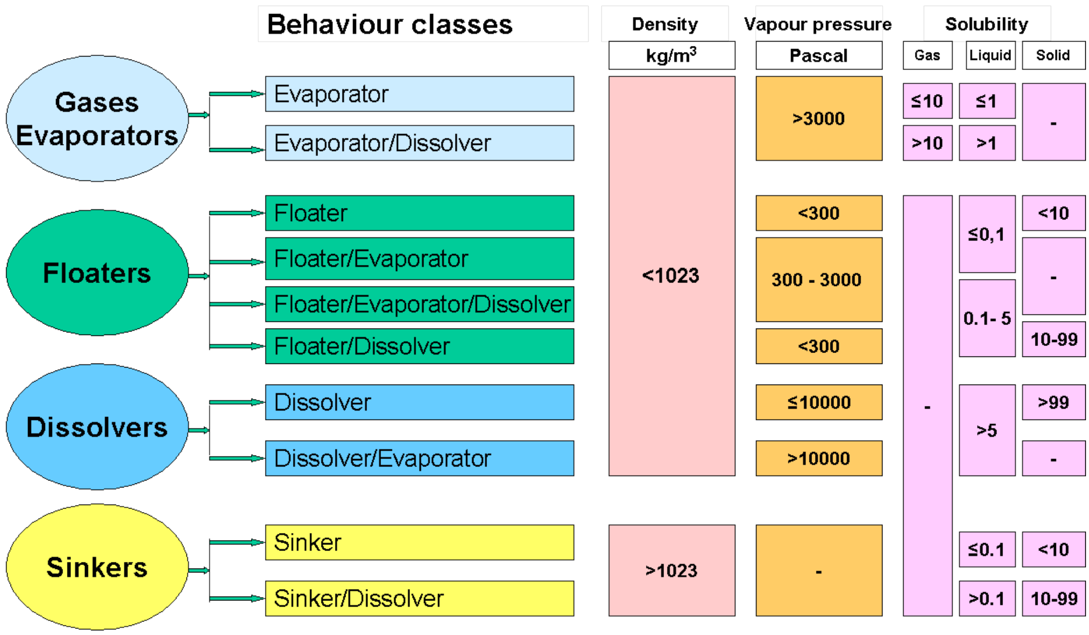

Figure 2.8.3 Categories of chemical substances and the physico-chemical characteristics (density, vapour pressure and solubility) on which the categorisation is based. The density is specified as 1023kg/m3, this might vary in different locations depending on the salinity.

Human populations as well as the marine environment can be exposed to spilled hazardous chemical substances. Ten potential hazards (including polymerization) can be distinguished when chemical substances enter the marine environment. The hazards are listed in Figure 2.8.4 and described accordingly for each behaviour category.

Potential hazards	Behaviour category *	Human health	Marine environment
Toxicity by inhalation	G/E/F	X	X
Explosiveness	G/E	X	X
Polymerization	G/E	X	X
Flammability	G/E/F	X	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

* G = Gases; E = Evaporators; F = Floaters; D = Dissolvers and S = Sinkers

Figure 2.8.4 Most relevant hazards of chemical substances within a behaviour category for humans and the marine environment.

Substances released into the marine environment could pass into the air (gas clouds), onto the water surface (floaters), into the water column (dissolvers), to the water bottom (sinkers), or a combination of these. Each behaviour has its own relevant hazard aspects. For example, toxicity to human populations and explosivity are typical hazard aspects of substances which pass into the air after a release.

Figure 2.8.5 gives some examples of chemicals in the different behaviour groups.

	Group	Properties	Examples
Evaporate Immediately (Gases)	**G**	Evaporate immediately	Propane, butane, vinyl chloride
	GD	evaporate immediately, dissolve	Ammonia
Evaporate Rapidly	**E**	float, evaporate rapidly	benzene, hexane cyclohexane
	ED	evaporate rapidly, dissolve	methyl-t-butyl ether vinyl acetate
Float	**FE**	float, evaporate	heptane, turpentine toluene, xylene
	FED	float, evaporate, dissolve	butyl acetate isobutanol ethyl acrylate
	F	float	Phthalates, vegetable oils, animal oils dipentene, isodecanol
	FD	float, dissolve	butanol butyl acrylate
Dissolve	**DE**	dissolve rapidly, evaporate	Acetone, monoethylamine propylene oxide
	D	dissolve rapidly	some acids and bases, some alcohols, glycols, some amines, methyl ethyl ketone
Sink	**SD**	sink, dissolve	dichloromethane 1,2-dichloroethane
	S	sink	butyl benzyl phthalate, chlorobenzene creosote, coal tar, tetraethyl lead, tetramethyl lead

Source Helcom, Manual on Co-operation in Response to Marine Pollution

Figure 2.8.5 Examples of chemicals in the different behaviour groups

The advantage of such an approach is that it limits the response action plans that need to be worked out, and there is no need for an action plan for each separate chemical substance. In addition, training courses on how to deal with chemical spills are simpler and do not require a thorough knowledge of chemical substances. As long as one can place a spilled chemical in the correct response category, it will be easier to take decisions on how to deal with the spilled substance.

Seven response categories are distinguished based on the behaviour class and the relevant hazard aspects (potential effects).

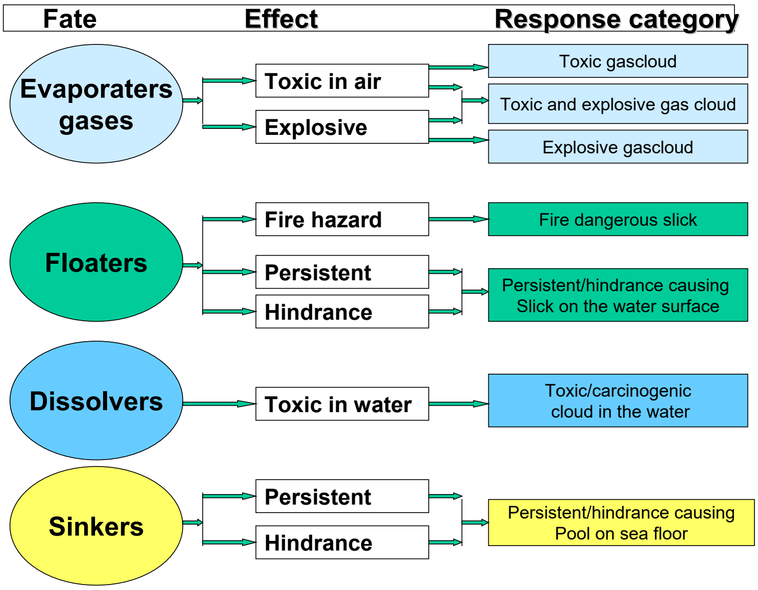

Figure 2.8.6 Summary of possible response categories

Lost packages could contain very dangerous substances which could escape into the water because of damage to the package or, in the long term, due to corrosion and therefore need to be recovered. Packages could float at a more or less level of submersion or sink at a more or less long term. Their potential danger is dealt with in the same way as bulk substances. It should be recognized, however, that packaged chemicals would always be present in smaller volumes than bulk chemicals.

A scenario which is not covered by the response categories based on behaviour and potential hazards is the scenario in which chemicals react or where there is a potential danger for reaction. Polymerisation, reactions between different chemicals on board, reaction of chemicals with water or reaction caused by heat or fire are some examples. In all such circumstances, decision making is more complex as experts are required to predict the possible consequences of such reactions not only to the environment but also to the ship's construction. Although a substance may not be particularly harmful in itself, the results of any reaction could be extremely dangerous. Information is therefore needed about the type of reaction products that are formed with water, acids, bases, metals, organic compounds, flammable substances, and oxidising and reducing agents. Other factors which must be taken into account when assessing the hazards associated with particular substances are the subsidiary phenomena that accompany these reactions, such as: formation of foam; formation of fog; change of colour; reactions in which poisonous or flammable substances are formed; fire; spattering; heat release.

It is of vital importance that people working in areas where dangerous chemicals are involved should be aware of the reaction risks involved.

This chapter further deals with the steps to be taken in the case of an accidental spills of hazardous materials other than oil, e.g:

- Notification/verification (see 2.8.3)
- Initial measures (see 2.8.4)
- Hazard assessment (Situation analysis) (see 2.8.5)
- Decision making (see 2.8.6)
- Response actions (see 2.8.7)
- A property glossary is given in section 2.8.10.

2.8.3 Notification and verification

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 reconnaissance, preferably by helicopter or airplane with an expert from the competent operational control authority. Information can also be obtained or verified through the agent of the vessel, and also through the port authorities of the last port of call or the port of destination. Later, if it is safe to do so, a response vessel can be brought close to the casualty for further inspection by trained experts.

A major problem at the initial stage of accidents involving hazardous materials is the lack of adequate information. Sometimes there is a problem in the precise identification of the cargo and loading plan. Much of the information contained in the initial report will be incorrect, and will need to be verified:

- obtain an accurate position for all vessels involved;
- confirm type and quantity of substances involved;
- confirm estimates of quantity of substance released;
- determine exact location of the released substance(s); and
- determine if reactions are likely (polymerisation, between chemicals or with water).

This should be done by: direct communication with the casualty vessel via radio link; aerial reconnaissance by helicopter and experienced observers; an expert team on board a vessel based close to the casualty or contacts with ship owners, cargo owners, last port of call etc.

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, water temperature and wind speed) have to be known, because these conditions will determine the fate and effects of a spill at sea.

The following are rules of thumb on how to determine the location of the spilled substance(s):

- **Gases or evaporators:** The cloud will travel in the general direction of the prevailing wind. It will tend to broaden and become more diluted the further it travels, lessening the toxicity risk. As regards explosivity, this dilution may increase the risk in the first minutes, as the Upper Explosivity Limit may be reached. . The danger-zone associated with the cloud will be roughly elliptical or teardrop in shape. From the point of release, the cloud will move with the actual wind speed in the prevailing wind direction in a triangular area with an angle of 30-60°. The area defined from a 30° angle is the danger zone. The 60° angle can be used as an additional safety factor.
- **Floaters**: From the point of release a slick will move at a rate of about 3% of the actual wind speed in the prevailing wind direction and 100% of the tidal current speed in the tidal current direction.
- **Dissolvers:** From the point of release the dissolved cloud in the water will move with the actual tidal current speed in the prevailing tidal current direction in a triangular area with an angle of 30-60°. The area defined from a 30° angle is the danger zone. The 60° angle is used as an additional safety factor.
- **Sinkers:** From the point of release the sinker will move with the actual current speed in the current direction as long it is submerged and not on the seabed. The sinking speed can be roughly calculated using Stoke's Law e.g. the sinking speed S (m/s) is a function of the gravitational force g (9,81 m.s-2) times the density differences between water and oil Δρ (kg.m-3) times the diameter size of the droplets/lumps d (m) to the power 2 divided by the dynamic viscosity of the water η (9.81x10-3 kg.m-1.s- at 20 ºC) times 18. The sinking time is the depth divided by the sinking speed.

The location and trajectory of a spill can be defined more precisely with the help of computer models. One should keep in mind, nevertheless, that these models do not, at this stage, take into account the reactivity of the product with water, with air, or with other products potentially involved. These models cannot either predict the behaviour of mixtures. When the response team is in the vicinity of a spill, more precise identification of the spill needs to be assessed. This can either be done visually or by measuring and sampling techniques.

2.8.4 Initial measures

The activation of emergency measures depends on the nature of the chemical, the source location and the prevailing weather conditions, taking into account local hydrodynamic and meteorological information. High priority has to be given to the protection of involved ship(s) crew(s) and the safety of passing ships and emergency measures in order to minimise or eliminate further outflow of hazardous substances.

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

- decide whether or not there is an imminent threat to important resources or to human health;
- ensure appropriate protection for the crews of involved vessels;
- ensure the safety of passing vessels;
- alert responsible and relevant authorities; and
- take necessary steps to minimise or eliminate further outflow.

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. Mathematical models should complement this calculation at a later stage in the incident as soon as more complete and accurate data becomes available.

Calculations for gas clouds

The worst case for gas clouds e.g. m^3 of air polluted will be: the estimated amount of chemical spilled (in mg) divided by the MAC (Maximum Allowable Concentration) value (in mg/m^3). To determine the area polluted one can assume an average height of the gas cloud of 10 m and divide the m^3 air polluted by 10. The potential for explosion must also be considered.

Calculations for clouds in the water column

The size (m^2) of the worst case cloud in the water will be the estimated amount of chemical spilled (in kg) divided by 1% of the LC_{50}(96) value (mg/l) of the chemical involved and divided by assumed average depth (m) at the spill location, assuming that the chemical is homogeneously dissolved in the whole water column .

Some initial response measures could be:

Stop or (partly) reduce release: The release can be either completely stopped or reduced. It is one of the most effective response methods if it can be applied. Since hazardous substances may be involved, response measures associated with the source of release may be particularly dangerous. Stopping the release and the overloading of cargo from the damaged tank/hold to an undamaged tank/hold or even to another vessel is one of the first options to consider. Holes in a damaged hull should be closed with the help of magnetic material, stoppers or any available material to close the hole. In the case of packages, nets can be used to prevent further losses and oversized drums can be used for damaged packages.

Change position of source: The main aim of changing the position of the source or cargo is to restrict the possible outflow or to reduce other hazards, simply by transferring the cargo (bulk or packaged goods) to a place where the threat posed by the substance is reduced. Methods applicable may include: removing containers from the deck; transhipping the cargo; towing the ship to a less vulnerable location.

Controlled release from source: Controlled release might be applied in order to reduce the dangers presented by the substance if there is risk of an uncontrolled release. Methods applicable may include destruction/explosion of the package or destruction/explosion of the ship. Jettisoning one or several containers can also be an option.

Containment/diverting substance: Containment and diverting substances or packages from their course may enable them to be collected more easily. This method may also be used to prevent their further movement. Methods applicable may include using containment booms or using chemical booms (herders).

In the initial phase of the response, in the case of a ship accident in which chemicals are involved or potential losses in the marine environment are expected, the necessary measures need to be taken as quickly as possible in order to reduce or limit the effects.

In the case of gas clouds, a warning for aerial operations should be issued as soon as possible with an indication of the no-fly zone and duration of the measure.

2.8.5 Hazard assessment

Risk assessments for the transport of chemicals and the hazard evaluation of a potential outflow must form part of the national ability to respond to major spills or pollution. The extent of the threat from the incident must be evaluated in order to identify the level and nature of response necessary.

The fate and effects of the released substance should be ascertained taking into account its behaviour, the local oceanography and meteorology, the proximity of sensitive organisms, habitats or resources, and their vulnerability to the chemicals involved.

Dividing the chemicals into different subcategories (G, GD, E, ED, FE, F, FD, FED, DE, D, SD, and S) leads to a need for a relatively small number of generally applicable response options in the event of an accident. It is important to be aware of the hazards that chemicals can cause when released into the marine environment. The most important aspect of situation analysis is determining the hazards of an accidental spill in order to prepare a plan of action.

In the event of an accident at sea, pollutants may contaminate the air, the water surface, the water column and/or the sea floor and, indirectly, all the organisms in these compartments and other users of these compartments. The degree of seriousness depends amongst others on the properties of the substance released and the fate and transport of the substance in the marine environment.

Gases or evaporators will evaporate fast after release in or on the water and will form a gas cloud in the air. A gas cloud can be toxic or explosive or a combination of these. Inhalation of a gas or evaporator by humans or marine organisms on or near the water surface can lead to respiratory toxicity or carcinogenicity. Dense gases (heavier than air) will disperse much more slowly than gases that are lighter than air. An appreciable number of a wide range of industrial chemicals regularly transported by sea could form poisonous gas clouds if released into the marine environment. The presence of such clouds would pose a considerable threat to all those in the area. A distinction can be made between the severity of the effects caused by exposure to toxic substances i.e.

- slight irritation, watering of the eyes and choking;
- serious irritation, which stops when exposure ceases;
- damage to health;
- reversible damage to health;
- irreversible damage to health;
- death.

In addition, the risk of dizziness/incapacitation should be considered, since it may lead to wrong decisions and expose operators/responders to other hazards (drowning, not being able to escape from a fire).

In the case of toxic gas clouds the inhalation risk presents the greatest hazard. The effect of exposure to toxins is principally determined by two factors (1) the period of exposure and (2) concentration in the atmosphere.

A vapour or gas cloud will drift with the wind, disperse and become diluted as a result of the turbulence in the atmosphere. The extent of the turbulence depends on the stability of the atmosphere and the roughness of the sea over which the cloud passes.

Floaters stay on the water surface for a certain period of time. The pollution effects include external coating (birds and mammals) or direct toxic action to marine organisms, inhibition of natural reaeration of the waterway, and restriction of recreational and water supply uses. Even more problems arise when such a spill reaches the coast or when such a spill occurs in wintering or feeding areas for birds. In winter, many species of birds are extremely sensitive and small spills of persistent floating substances can affect the functioning of thousands of birds. Mammals can be smothered by a floating chemical, which can affect their respiratory system. However, mammals mostly tend to flee from floating layers of substances.

There are two main hazards potentially associated with floaters: fire and dangers due to natural dispersion in the water column affecting the aquatic environment. Moreover, floaters may drift on the wind or current and can reach sensitive areas along the coast or wetlands. Little damage to fish is likely to be caused by hazardous substances as long as the substance floats on the surface. More problems arise when a spill occurs in or reaches shallow waters or when a spill happens in the breeding season for mammals and birds. Mariculture (fish cages, oyster beds….) may also be affected by floating slicks.

Dissolvers are substances which will quickly dilute into the water column after release. The greatest danger caused by dissolvers, due to their aquatic toxicity, is a high concentration of the hazardous substance in the water during the escape phase. In the open sea, the most seriously threatened animals are mammals (seals, porpoises, etc.), pelagic fish (herring, sprat, etc.) and zooplankton (especially larvae and eggs). In the open sea, however, most of the chemical will dilute quickly and a “no effect concentration” will soon be attained. Exceptions to this dilution phenomenon are the bio-accumulative and persistent substances that even at low concentrations must be considered harmful. Many fish species have rather restricted spawning areas in open sea, or in coastal areas. From there, eggs and larvae are transported with the currents to specific nursery areas. Often these nursery areas are productive tidal areas along the coast, such as estuaries. Spills in these areas may cause severe losses to the population, because the juvenile stages are generally much more sensitive than the adults and also occur in more concentrated numbers. Some dissolvers will also induce a variation in the pH, which should nevertheless be, in open seas, compensated by the buffering power of seawater.

A dissolved chemical concentration in the water may have lethal effects. The higher the exposure concentration, the shorter the time it takes before lethal effects appear. In an actual spill situation the concentration in the water is not constant and will also decrease over time due to dilution in the water. Dissolved chemicals may cause acute effects if the concentration exceeds a certain level for a certain exposure time. At low concentrations, and/or at short exposure times, only limited effects may be expected.

Knowledge of water mixing characteristics will result in a better understanding of the risks to aquatic ecosystems as a result of acute pollution into the water column. The theoretical concentration of a particular spill scenario, assuming that the chemical has been dissolved into the water, can be calculated (Predicted Environmental Concentration (PEC)) and compared with toxicity effect threshold concentrations as given in 2.8.4.

Dilution of chemicals in estuaries and seawater is predominantly dictated by oscillations from wind and tide currents. The concentration in the water depends primarily on the mixing capacity (dilution rate) of the water body.
Due to the turbulence of the receiving water, the chemical will dilute in all directions and will at some point reach levels where no effects will occur. Hence, knowledge about the range and degree of mixing in relation to local hydrology is important for establishing criteria and standards that can be used for the risk assessment of dissolved substances.

The concentration primarily depends on the amount of substance spilled, and on the depth of the water. Secondly, the horizontal spread of the dissolved substance in the water determines the dilution and by that the concentration as a function of time. As a consequence, the initial concentration will be high, but the number of exposed organisms is limited, while later on there will be an enormous increase of exposed organisms due to the increased volume of water containing the diluted substance, but only at a much lower exposure concentration.

Spills in this group (Dissolvers) lead to a cloud/plume of dissolved substance that will drift away with the current. Often it is assumed here that organisms are exposed continuously to the cloud/plume, and that the concentration decreases in time as a result of dilution. This is a conservative assumption, since only planktonic organisms (algae, zooplankton) are transported with the water current; benthic organisms are fixed at one place and will only be exposed for the time it takes the polluted water volume to pass; for mobile organisms like fish, the exposure time is rather unpredictable, but will be shorter than 'continuous'.

In waters with a high mixing energy, such as the North Sea, the risk of dissolved substances is much lower than in low mixing waters such as harbour areas. The PEC in the water column is determined by the initial dilution over the water column (from water surface to water bottom or mixing depth) followed by a horizontal dilution factor depending on specific hydrological conditions of the receiving water body.

Sinkers are substances that will sink to the seabed due to their density and stay on the sea floor for a certain period. Sinkers are generally hazardous to the marine environment due to aquatic toxicity, whereas direct danger to human beings is very limited. In the open sea, the most sensitive areas are the spawning grounds. Chemical spills may directly affect benthic fish and their predators. Mammals avoid pollution by sinkers and, therefore, mammals will be affected minimally. Pelagic fish also share this mechanism by avoiding pollution. Problems could occur when large quantities of bulk substances are released on the seabed. The major effect in such cases is the blanketing of the seabed, thereby covering the zoobenthos. The contribution of zoobenthos to the biomass of the food chain is prominent in coastal waters and intertidal zones. Spills in these waters can, therefore, cause severe losses to zoobenthos and if the spill penetrates the sediment by bioturbation or otherwise, losses may occur over long periods.

2.8.6 Decision making

Once an accidental spill has occurred, the type and degree of damage to human health and the marine environment will to a considerable extent be a matter of chance. The type and degree of damage depends partly on fortuitous circumstances and partly on the actions taken to minimise damage. Each spill will have its own detrimental effects in the aquatic environment. The damage may range from insignificant to catastrophic. The primary aims of a chemical substance spill response are to:

- protect human health and safety;
- minimise environmental impacts; and
- protect amenities; and
- restore the environment, as far as is practicable, to pre-spill conditions.

The range of counter pollution measures to be applied will depend upon the location of the spill, type and quantity of the pollutant, the environmental sensitivity and biodiversity of the area affected. Good management and planning, as well as the response actions put into effect by the responsible authority can minimise the environmental impact of a chemical or hazardous substance spill.
Decision-making systems must be based on adequate information about: (1) Hazard analysis (kind of substance released, reaction ability, behaviour, potential outflow and potential impact) and (2) Response options (methods and techniques for minimising input and recovery of released substances; measures for maintaining safety of navigation; alerting measures for safety of adjacent populated areas and appropriate protection for response teams). The Mar-ICE service, deployed by EMSA, can be useful at this stage.

Decision-making must incorporate an evaluation of the threat posed by the released chemical to human health and the marine environment and related interests. Before decision-making can start, the following information about the (potential) spill(s) needs to be known:

- the behaviour category and/or sub categories
- the potential hazards
- the ability to reaction (e.g. polymerisation, reaction with water or with air etc)
- the spill location and predicted trajectory.

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 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. Exclusion zones (water, land, air) can be established at this stage.

After the seriousness of the spill has been determined there are two possibilities:

(i) Impact likely: response actions need to be taken; or

(ii) Impact not likely: no response actions needed (always keep monitoring).

The main factors on which the selection of response methods is based are the physical behaviour of the substances released and the relevant hazard aspects.

Based on the damage estimations, the nature, extent and the long-term effects of the chemical contamination, the following steps have to be taken in accordance with the National Contingency Planning:

- Once the hazards has been evaluated, the appropriate teams should be activated promptly. Early advice to coastal authorities might now need to be adjusted, as well as exclusion zones.
- Alert or warn - if necessary – the adjacent population (with possible evacuation or sheltering instructions) with particular regard to beach resorts; local authorities competent for counter measures; ships traffic by broadcasting navigational warnings; fishing boats and fishing harbours. In serious cases evacuation of threatened population from restricted areas.
- Alert skilled personnel, well trained to overcome safety problems during recovery, cargo transfer or lightening operations, i.e. fire brigade, civil defence corps, salvage operator, chemical industry.
- Mobilise adequate recovery or lightering equipment. Contact tanker owners if lightering capacity is needed for cargo transfer or temporary storage of chemical-water-mixture.
- Ensure a safe and continuous management at sea by:
    - demanding ships and airplane/helicopter for monitoring at sea and aerial surveillance/assistance at recovery
    - contact tanker owners if lightening capacity is needed for cargo transfer or temporary storage of chemical-water-mixture
    - initiate precautions by delimitation of restricted or prohibited areas to ensure safety of navigation and continuous recovery or cargo transfer
    - preparation of land based confined areas for containment of recovered substances, mixtures or packaged chemicals
    - availability of suitable storage tank capacity for the disposal of liquid substances or mixtures
- At the scene, the On-Scene-Commander must ensure: continuous measurements of atmospheric concentrations; detection of toxic contaminants, explosive, combustible atmosphere or vapours;

detection of other harmful gases or vapours; suitable protective clothing and respiratory equipment; suitable over-packs for damaged or leaking packages containing harmful substances.

- Request for personnel or technical assistance is advised if national forces and services cannot cope with the chemical disaster and its effects on strike teams and the marine environment.

The selection of the response method is highly dependent on the nature of the spill, the local circumstances, weather conditions, availability of and accessibility to equipment, and the properties of the pollutant. In addition to the criteria mentioned, political considerations can play a prominent part in decision-making. Sometimes it is difficult to assess which response technique is most suitable for the spill concerned. The first priority is always to ensure the safety of those involved in the spill clean up. The second priority is to remove as much as possible of the pollutant without causing any further damage to the marine environment.

If it has been recognised that removal of the substance from the environment is not necessary or possible, then consideration should be given to establishing a monitoring regime around the area likely to be affected. The objectives of the monitoring should be to alert the authorities to a release of the chemical into the environment, to provide information on the extent of the release and the behaviour of the chemical, and to measure its impact on the adjacent environment. Water, sediments, air and biota might need to be sampled and analysed depending on the particular circumstances, which will also dictate the necessary spatial and temporal distribution of the samples.

Considerable expertise is necessary to set up a monitoring programme that will meet the objectives without unnecessary expense. An occasional sample from the water column or seabed near the wreck will rarely be of any value.

Monitoring and measuring of spills at sea is one of the most essential parts of response to accidents involving chemicals, not only to determine the seriousness of the spill, but also to determine when the situation is safe again. In contrast to oil, chemicals are often invisible once released into the marine environment or into the air. For the detection of the various chemicals, different methods are required to measure the concentration (in the air or in the water column) or the size and layer thickness (on the water surface or on the seabed).

Computer models are useful for determining the right location to measure and to predict the concentration in case measurement is impossible due to lack of measuring equipment or lack of time. On the basis of computer prediction, or rule of thumb, one should determine the place to do the measurements and/or sampling. Obviously near a ship in distress one should take measurements continuously, but once the spill is released, computer predictions are necessary as the cloud or slick will move due to external factors such as wind and/or current.

Remote sensing aircraft normally used for oil detection can also be used for floating slicks of chemical spills. For sinkers, ROVs or divers need to be used to locate the pool of hazardous substance on the sea floor. To measure concentrations in the air and in the water column, a vessel needs to go on scene with the appropriate measuring and sampling tools.

2.8.7 Response actions

Depending on the situation, response actions could be applied to:

- the ship itself (evacuating, extinguishing or reducing the fire, towing, sinking, refloating...)
- the cargo (moving on board, extinguishing or reducing the fire, destroying jettisoning, pumping,...)
- the pollutant, i.e. HNS released on board or overboard (marking, detecting, dispersing, containing, recovering...)

Beyond the response at sea and except in the case of an incident within a harbour, the issue of the identification of a safe heaven/port of refuge will arise very quickly.

The ship: in case of fire on board, the presence of contaminated extinguishing waters could create a double problem: the increase in draught (for the MSC Flaminia, with 30000 tons of polluted waters, the draught increased from 14 to 20 m) and difficulties to identify a suitable port of refuge and secondly the need to treat polluted waters, which cannot be released at sea.

The cargo: as an example, containers containing a substance (S/E) which is highly dangerous by inhalation could be jettisoned.

The aim of a counter pollution action is to reduce or eliminate the hazardous effects of a spill. The choice of the most appropriate counter pollution action depends on the behaviour and the dangers of the substance released. For measuring/detection purposes, as well as for response, a distinction can be made between the following response categories:

1. Toxic gas clouds
2. Toxic and flammable or explosive gas clouds
3. Flammable or explosive gas clouds
4. Fire dangerous slicks
5. Persistent/hindrance causing slicks on the water surface
6. Toxic/carcinogenic clouds in the water column
7. Persistent/hindrance causing pools on the sea floor

Another category of response is “(Sunken) packaged goods or complete vessels containing chemicals”. This category is different from the seven mentioned above where the risk is associated with the substance and its behaviour. It has to do with the way hazardous substances accidentally enter the marine environment, irrespective of their characteristics and risks. It therefore will be dealt with separately. Each response category will be discussed in the following paragraphs.

Toxic and/or explosive gas clouds: this group of chemicals can rarely be combated at sea. Response to this group of chemicals is mostly limited to reducing exposure to the chemicals by restricting access to the area of trajectory of the gas cloud. Appropriate computer models are useful to predict the size and trajectory of such a gas cloud in combination with on-scene concentration measurements. The cloud can be made visible by giving it a colour using specific reagents. When clouds are made visible, the exact position, dimensions and track can be followed much more easily.

For **toxic gas clouds** a comparison with the Maximum Allowable Concentration (MAC) values or Threshold Limit Values (TLV) of the substance(s) could be used as an indication of the seriousness. If the concentration is less than 10% of the MAC/TLV the situation can be assumed to be safe again. PAC (Prediction Action Criteria can also be used. Use of protective clothing/breathing apparatus and (partial) evacuation can be considered as possible response options. When skin contact with a dangerous substance is inevitable or likely to happen, preventive counter measures should be taken in the form of special body protection clothing. Breathing apparatus can be used for the protection of the respiratory organs if disagreeable or toxic gases are released. Breathing apparatus can be worn in combination with other protective clothing.

For **explosive gas clouds** a comparison with the Lower Explosion Limit (LEL) value of the substance(s) could be used as an indication of the seriousness. If the concentration is less than 1% of the LEL concentration the situation can be assumed to be no longer explosive. Also take into account the UEL (Upper Explosive Limit) that can be reached after some time, when the initial concentration decreases.

All sources of ignition that may cause ignition of a flammable or explosive material must be removed. This makes it impossible for an explosion or combustion to take place. Possible sources of ignition are electric apparatus, hot surfaces, , naked flames and sparks, etc.

As a rule of thumb, when the concentration of a gas in the air is over 1% of the LEL, care must be taken in order to avoid an explosion. The concentration at which the gas cloud could be toxic is much lower than the concentration at which a gas cloud could be explosive.

Fire dangerous slicks: This group of chemicals can be combated with the so-called first line oil recovery vessels. As this group of chemicals is fire and explosion dangerous the explosivity potential needs to be continuously measured during the recovery actions.

Due to evaporation, this kind of spill will disappear from the water surface after some time. For this group, computer models are useful to predict the seriousness, the size and potential trajectory of the slick, the length of time it will take the slick to disappear from the water surface if only partial recovery or no recovery takes place.

Controlled combustion is a possibility to be considered if the substance layer is of sufficient thickness (> 3 mm). The risk associated with this method is high. The reaction products should be known and people should maintain a safe distance from the source. The weather conditions should be suitable.

Sampling, monitoring and calculations with the aid of models can estimate the size of the threatened area. Access to the polluted area has to be restricted as long as the concentration is higher than 1 % of the LEL value. Activities in the area, which can cause ignition, may also have to be restricted. Once the area is declared safe the restriction should be lifted.

When skin contact with a dangerous substance is inevitable or likely to happen, preventative counter measures should be taken in the form of special body protection clothing. It is safe to recover the substance when the concentration in the air measured on board the recovery vessel is less than 1% of the LEL. One should never go into a polluted area (slick) when the gas concentration is too high, not even with a first line recovery vessel.

26.6.13 **Persistent/hindrance causing slicks on the water surface:** This group of chemicals can be combated with oil spill response means such as skimmers, booms and sweeping systems. For the safe recovery from the water surface of chemical substances with a flash point < 61 º C, only vessels complying with tanker regulations (so called first line oil recovery vessels) should be used.

As a lot of floaters are invisible to the naked eye, remote sensing tools need to be used to detect such slicks on the water surface. For this group, computer models are useful to predict the seriousness and the potential size and trajectory of the slick. Floating buoys that follow the same drift pattern than the product and that are traceable by satellite may also be useful.

Mechanical recovery involves the containment of the floating pollutant and removing it from the sea surface by means of: skimmers, sweeping systems and, in the case of very viscous or solid substances, netting. Although there are many different types of skimmers and other recovery devices to remove oil from the water surface, the choice of response equipment depends on the type of chemical (viscosity, corrosivity etc.) released.

Toxic/carcinogenic clouds in the water column: This group of chemicals, once released into the water and dissolved, cannot be recovered at sea. Response to this group of chemicals is limited to reducing exposure to the toxic effects of the substance by restricting access to the area of trajectory of the cloud. This needs appropriate computer models to predict the size and trajectory of such a cloud in the water column, the time period it will take to affect benthic habitats, in combination with on scene measurements Portable detection systems such as DeltaTox ® analysers can be used.

The spill (cloud in the water column) can be given a colour/tracer in order to make it visible. This can be done using specific reagents. When clouds in the water column are made visible the exact position, dimensions and track can be assessed much more easily.

Sampling and calculations with the aid of models can estimate the size of the threatened area. Access to this area has to be restricted. Activities in the area may also have to be restricted. Once the area is declared safe, the restriction should be lifted.

A concentration of a toxic substance can have one of these three effects on organisms:

- no effect; this level is normally taken as 1% of the LC50(96);
- a sub lethal effect (for example, inhibition of growth); and
- a lethal effect (LC50(96).

The effects on organisms depend on many factors (kind of organism, exposure time, the condition of the organism, etc.). The situation can be assumed safe again when the concentration is < 1% of the GESAMP B1 rating or the LC_{50}(96) of the substance involved.

The toxic effect of a "Dissolver" will be more serious if the substance is bioaccumulative and/or persistent (does not easily biodegrade in the marine environment). The effect of a chemical in the marine environment is a combination of the concentration and the exposure time to organisms living in the water. The higher the concentration the more serious the effect (e.g. bioaccumulation increases the concentration in the organisms exposed and so increases the effects). The longer the exposure time the more serious the effect of a chemical will be (e.g. chemicals which are non-biodegradable, or slowly biodegradable, will stay longer in the marine environment and so increase the exposure time resulting in more serious effects).

Persistent/hindrance causing pools on the sea floor: substances in this group will stay on the sea floor giving some time to react and to determine the best combating option. This group of chemicals can theoretically be combated with existing dredging equipment. The best solution for dealing with this category of sunken chemicals needs to be determined on an *ad hoc* basis. Availability, depth, type of substance and many other factors will determine which dredging tools will suit best.

Dredging is usually described as a system for the removal of underwater material. Therefore it can be used as a response method for substances that are heavier than water. A choice can be made between hydraulic, mechanical and pneumatic dredgers. The use of vacuum units is an alternative response method. Before starting recovery operations, methods of storage and removal of the collected substances must be evaluated.

Detection of sunken substances could cause problems,. ROV and/or divers could be needed. In some cases, products may be located and mapped using acoustic imagery by deploying both a side-scan sonar and multibeam echosounders (to simultaneously acquire data on the depth and nature of the bottom). Computer models could assist in finding the place where the sinker will rest.

Sampling and calculations with the aid of computer models can estimate the size of the threatened area. Access to the area has to be restricted. Activities in this area may also have to be restricted. Once the area is declared safe the restriction should be lifted.

Immobilising a substance by burying it will prevent further movement of the substance. It is a mechanical method which leaves the substance in the environment. Therefore the need to remove the substance from the seabed should be evaluated. This option is possible only in areas where there is no or very slow currents.

(Sunken) packaged goods or complete vessels containing chemicals: There are several salvage techniques to recover packages and sunken vessels from the sea floor. It is not the substance in the package or ship that determines the best response option but factors such as water depth, strength of the package/ship and current. As is the case with sunken substances (sinkers), the major problem is the detection of packages on the sea floor. Once found, salvage companies have the ability and the required skills to remove the packages. During salvage operations one should always be prepared for the possibility that the packages/ships might break and that substances could be released into the marine environment. Depending on the category the substance(s) belongs to, one of the above-mentioned measures should be taken.

Many liquid chemicals are transported in 200-litre steel drums. Figure 2.8.7 shows the typical data for such drums that can be used when calculating the buoyancy in water when filled with various chemical liquids. Figure 2.8.8 and Figure 2.8.9 show results from such calculations and indicate when drums might float or sink. Figure 2.8.8 gives examples of low density liquid chemicals which are often carried in 200-litre steel drums, and which, due to their density, will cause the drums to float in water. Figure 2.8.9 gives examples of high density liquid chemicals which, due to their density, will cause the drums to sink in water.

NB: Cans and drums filled with solid chemicals will always sink in water.

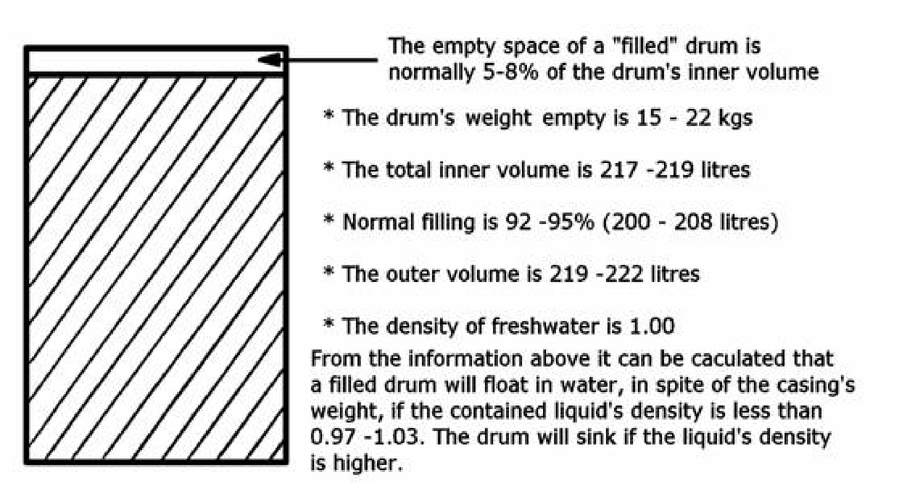

Figure 2.8.7 Calculating the buoyancy of drums

Types of chemicals	Examples
Hydrocarbons	hexane, benzene, toluene, xylene
Alcohols	methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol
Ketones	acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone, cyclohexanone, methyl cyclohexanone
Ethers	diethyl ether, ethyl butyl ether
Esters	methyl acetate, ethyl acetate, butyl acetate
Amines	monoethylamine, diethylamine, ethylene diamine, diethylene triamine, diethylene tetramine
Aldehydes	formaldehyde, acetaldehyde, butyraldehyde, acrolein

Figure 2.8.8 Examples of low density liquid chemicals which, due to their density, will cause the drums to float in water.

Types of chemicals	Examples
Acids	acetic acid, acrylic acid, formic acid, phosphoric acid, sulphuric acid
Bases	sodium hydroxide solution, potassium hydroxide solution
Glykols	ethylene glycol, diethylene glycol, propylene glycol
Chlorinated hydrocarbons	carbon tetrachloride, trichloroethylene, tetrachloroethylene, methylene chloride, ethylene dichloride, trichloroethane
Miscellaneous	carbon disulphide, toluene diisocyanate, tetramethyl lead, tetraethyl lead

Figure 2.8.9 Examples of high density liquid chemicals which due to their density will cause the drums to sink in water

2.8.8 Summary

Risk assessments for the transport of chemicals and the hazard evaluation of a potential outflow must form part of national ability to respond to major spillages at sea.

In the present situation:

- Floating substances, presuming that the necessary safety precautions have been taken, can mostly be combated with the help of first line oil recovery vessels and other oil response equipment (booms, skimmers and/or dispersants);
- Sunken substances can be recovered with dredging equipment; and
- Lost cargoes and sunken ships can be recovered by salvage companies.

However for the most common response categories, the Evaporators (gas clouds) and the Dissolvers, there are hardly any recovery techniques available and there is no time available for response at open sea. Response measures will be limited to restricting access to the threatened area while the substance dilutes naturally and the situation becomes safe again. Once the area is declared safe the restriction should be lifted.

Natural dilution of a gas cloud in the air or a dissolved cloud in the water column will decrease the concentration and therefore the seriousness of the release. On the one hand the concentration will become lower, but on the other hand the area polluted will become larger.

In all cases of chemical spills, the use of computer models is essential: (1) to determine the actual location; (2) to select the location for on-scene measurements; (3) to select the location for taking samples; (4) to determine the seriousness; (5) to predict the trajectory; and (5) to determine the mass balance.

Ships in distress containing chemicals need to be given special attention in national contingency plans. Such ships could contain several different chemicals still on board but which could enter the marine environment if the ship sank or broke. A critical decision will need to be made between, on one hand bringing such a ship in distress to a sheltered place (in order to repair the damage or to unload the cargo) or on the other hand, sending the ship as far away from the coastline as possible. Next to safety, economic and environmental factors play a role in this decision.

In the case of sunken packages, the environmental consequences of the release of its contents determines the need to recover such packages. Determining the solution rate per time unit sometimes requires experiments as such information is not available and is required to predict the possible environmental consequences. Submerged and floating packages/containers containing chemicals always need to be salvaged independently from their content as such packages form a collision danger for shipping and could wash ashore.

Contracting Parties to the Bonn Agreement should be informed in accordance with Article 5 of the Agreement (see Chapter 29 of this Manual). Request bilateral assistance within the framework of bilateral plans or other conventions for co-operation, or request multilateral assistance within the framework of the Bonn Agreement.

Requests for experienced personnel and specialist expertise should be made through:

- Mar-ICE
- CECIS
- ERCC in Brussels.26.7.8 Note: Requests for personnel or technical assistance is advised if national forces and services cannot cope with the chemical disaster and its effects on strike teams and the marine environment.

2.8.9 Background information

Further details and background information is provided in the IMO Manual on Chemical Pollution: Section 1 “Problem Assessment and Response Arrangements”, Section 2 “Search and Recovery of Packaged Goods Lost at Sea” and The revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by ships.

All EU projects dealing with response to chemical spills were inventoried in the framework of the Mariner project. Projects names and descriptions can be found here: http://knowledgetool.mariner-project.eu/projects. Outputs of some of these projects are here: http://knowledgetool.mariner-project.eu/resources

2.8.10 Property glossary

The properties listed are those which will provide an indication of a spilled chemical's environmental behaviour, effects and possible counter pollution actions.

Bioaccumulation

Continued retention of a substance in the tissue of an organism throughout the course of its existence (the bioaccumulation factor increases all the time).

Bio amplification

Retention of a substance in the tissue at increasingly higher concentrations the higher one goes in the food chain.

Bio concentration

Retention of a substance in the tissue of an organism to the extent that the content of the substance in the tissue exceeds that found in nature at one point in time of the lifetime of the organism.

Bio concentration factor (BCF)

According to EPA guidelines, "the BCF is defined as the ratio of chemical concentration in the organism to that in surrounding water. Bio concentration occurs through uptake and retention of a substance from water only, through gill membranes or other external body surfaces. In the context of setting exposure criteria it is generally understood that the terms "BCF" and "steady-state BCF" are synonymous. A steady-state condition occurs when the organismis exposed for a sufficient length of time that the ratio does not change substantially."

Flash point

The flash point refers to the lowest temperature at which a liquid still gives off enough vapour to be capable of ignition. The ignition source supplies an amount of energy, which is necessary to heat an explosive or flammable vapour, or gas mixture locally to a given temperature, which will produce an explosion or fire. This local temperature is referred to as the ignition temperature, which is dependent on the oxygen concentration, time, pressure and the presence of catalysts.

GESAMP (The GESAMP/EHS Working Group was established in 1974 to evaluate the environmental hazards of harmful substances carried by ship and provide related advice, as requested, particularly by the International Maritime Organization (IMO).

A-value hazards profile The GESAMP bioaccumulation ratings are a means of ranking the likelihood that particular substances become concentrated in living organisms.

+ = bioaccumulative to a significant extent and known to produce a hazard to aquatic life or human health;
Z = bioaccumulative with an attendant risk to aquatic organisms or human health, but with a short retention time of the order of one week or less;
T = bioaccumulative, liable to cause tainting of seafood;
0 = no evidence to support one of the above ratings.

B-value hazards profile The GESAMP ratings for assessing damage to living resources specified are defined below.

	96 hr TLm	
4 = highly toxic	< 1	mg/l
3 = moderately toxic	1 - 10	mg/l
2 = slightly toxic	10 - 100	mg/l
1 = practically non-toxic	100 - 1000	mg/l
0 = non-hazardous	> 1000	mg/l

D = substance likely to blanket the seabed
BOD = substance with oxygen demand

C-value hazards profile The oral intake rating describes the hazards posed to human health due to the oral intake of certain substances. Three categories of hazard can be distinguished.

2 = hazardous
1 = slightly hazardous
0 = non-hazardous

E-value hazards profile The GESAMP reduction of amenities rating. The effects that substances are likely to have on the availability of amenities can be rated in the following manner:

*** = highly objectionable because of persistence, smell or poisonous or irritant characteristics. As a result, beaches are liable to be closed. Rating also used when there is clear evidence that the substance causes cancer in human beings;
** = moderately objectionable because of the above characteristics. Short-term effects lead to temporary interference with the use of beaches. Rating used when there is credible evidence that the substance is an animal carcinogen, but when no clear evidence is available to suggest that the substance causes cancer in human beings;
* = slightly objectionable, non interference with use of beaches;
0 = no problems envisaged.

IMDG-Code Maritime Organisation Dangerous Goods (IMDG) Code. The International Maritime Organisation (IMO) approved a system of classifying chemical substances on the basis of the physical hazards involved at the International Conference on Safety of Lives at Sea in 1974. The IMO classification, given below, is an internationally recognised standard, which has been accepted in virtually all countries.

Class 1 explosives

Class 2	gases: compressed, liquefied or dissolved under pressure
Class 2.1	inflammable gases
Class 2.2	non-inflammable gases
Class 2.3	poisonous gases
Class 3	inflammable liquids
Class 3.1	inflammable liquids: low flash point group. Flash point below -18 °C, or possessing a low flash point in combination with other dangerous properties apart from inflammability
Class 3.2	inflammable liquids: intermediate flash point group. Flash point of -18 °C up to, but not including, 23 °C
Class 3.3	inflammable liquids: high flash point group. Flash point of 23 °C up to and including 61 °C
Class 4.1	inflammable solids
Class 4.2	substances liable to spontaneous combustion
Class 4.3	substances emitting inflammable gases when in contact with water
Class 5.1	oxidising substances (agents)
Class 5.2	organic peroxides
Class 6.1	poisonous (toxic) substances
Class 6.2	infectious substances
Class 7	radioactive substances
Class 8	corrosives
Class 9	miscellaneous dangerous substances

$LC_{(50)}$

Lethal concentration fifty $LC_{(50)}$ is a calculated concentration which is expected to kill 50% of the population of experimental animals. Dosage is the most important factor in determining whether a given hazardous substance will produce a toxic effect. For comparisons of the toxicity of different hazardous substances, the median lethal concentration LC(t)50 (t = 96 hours), is normally used as a yardstick. The higher the LC(t)50 value, the lower the hazard.

description	**LC(96)50 values**	
Highly toxic	< 1	mg/l
Moderately toxic	1 - 10	mg/l
Slightly toxic	10 - 100	mg/l
Practically non-toxic	100 - 1000	mg/l
Non-hazardous	>1000	mg/l

Mortality of an organism is a clear measure. With experiments the percentage of a specific kind of organism which dies within a certain time can be measured. For example LC-50 (96): The Lethal Concentration for 50 % of the test organisms within 96 hours. Other percentages (n) and exposure times (t) are possible (LC-n (t)).

LEL

The Lower Explosion Limit (LEL) is determined as the minimum percentage of vapour (gas) at which a vapour or gas mixture can be made to explode. Below the lower explosion limit, reaction only takes place when there is a continuous supply of external heat. In the case of concentrations above the lower explosion limit, combustion may occur.

MAC

The Maximum Allowable Concentration (MAC) of a substance given in ml/m^3 = ppm or mg/m^3 is defined as the maximum concentration of that substance in ppm of air in which people can work safely for a period of eight hours, five days a week.

Minimum hazard	- substances with a MAC	>500 ppm
Some hazard	- substances with a MAC	>100 <500
Moderately hazardous	- substances with a MAC	>10 <100

Severely hazardous - substances with a MAC <10 ppm
For substances with a very low MAC value, one should be very careful even if the substance is not classified as "Evaporator"

Marine pollution Category .

MARPOL Annex II Regulations for the control of pollution by noxious liquid substances in bulk sets out a pollution categorization system for noxious and liquid substances. The four categories are:

Category X: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, 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: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a hazard to either marine resources or human health or cause harm to amenities or other legitimate uses of the sea and therefore justify a limitation on the quality and quantity of the discharge into the marine environment;

Category Z: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, 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

Other Substances: substances which have been evaluated and found to fall outside Category X, Y or Z because they are considered to present no harm to marine resources, human health, amenities or other legitimate uses of the sea when discharged into the sea from tank cleaning of deballasting operations. The discharge of bilge or ballast water or other residues or mixtures containing these substances are not subject to any requirements of MARPOL Annex II.

The annex also includes a number of other requirements reflecting modern stripping techniques, which specify discharge levels for products which have been incorporated into Annex II. For ships constructed on or after 1 January 2007 the maximum permitted residue in the tank and its associated piping left after discharge is set at a maximum of 75 litres for products in categories X, Y and Z (compared with previous limits which set a maximum of 100 or 300 litres, depending on the product category).

No Effect Level When a toxicity experiment for sub-lethal effects is done, it is possible to find the so-called "No Effect Level". The 96 hour LC_{50} gives an indication of the concentration which, if exceeded, will be lethal; it is available for a wide range of chemicals and can be used to predict likely safe concentrations. Where a chemical spilled in the marine environment is neither persistent nor bioaccumulative, then acute, chronic or sub-lethal effects are rarely seen in organisms at concentrations of less than 0.01 times the 96 hour LC_{50} to the test species. In the absence of counter-indications, therefore, 1% of the LC_{50} can be taken as a "safe" No Effect Level (N.E.L). (see also No Observed Effect Level).

No Observed Effect Level No Observed Effect Level (N.O.E.L). It is possible to apply a conservative safety factor of 0.01 in translating acute L.C.(50) values to life cycle no-adverse-effect level. This still provides a large margin of safety between exposure limits and effect levels. (See also “No Effect Level”).

Octanol-water partition coefficient

The ratio of concentration of the chemical at equilibrium in octanol and water phase is related to bioaccumulation. The experience with a wide variety of organic compounds indicates that if this partition coefficient exceeds 1000, the probability of measurable bioaccumulation in aquatic species is high. Often this is expressed in Pow, the logarithm of the octanol/water partition coefficient, which gives an indication on the lipophylity rate of a chemical. When a chemical has a Pow larger than 3 or 4 (1000 to 10 000 as it is the Logarithm), it is able to pass the liphophyd membranes of the cells and accumulate in the fat resources. Not only bioaccumulation, but also sediment bonding can be described with the Pow values. A high rate of bonding to the sediment is related with a high Pow.

Relative gas density

The densities of the common gaseous products transported by sea are mostly given in kg/m^3. By comparing the density of a particular gas with that of air (1.29 kg/m^3), an estimate can be made of whether the substance will rise into the atmosphere or tend to remain on the water surface. The value obtained is equal to the ratio of the weight of a given volume of vapour to the weight of an equal volume of dry air at the same conditions of temperature and pressure. Using the ratio M/29, where M is the molecular weight of the substance concerned, may approximate this.

$TLM_{(96)}$

Tolerance Limit median, See LC_{50}

highly toxic	TLm less than 1	mg/l
moderately toxic	TLm 1 - 10	mg/l
slightly toxic	TLm 10 - 100	mg/l
practically non toxic	TLm 100 - 1000	mg/l
non-hazardous	TLm more than 1000	mg/l

TLV

Threshold Limit Values refers to an airborne concentration of a product expressed in parts per million by volume in air. This is the time-weighted concentration believed to be safe for the average person during an 8-hour workday and 40-hour working week for prolonged periods. The equilibrium concentration of a gas, which can be produced by a liquid, can be calculated as follows:

Concentration (ppm) = vapour pressure in mm of Hg x 1300 or
Concentration (ppm) = vapour pressure in Pa x 9.75
If concentrations are higher than three times the TLV level, warnings should be issued of possible health risks for people in the area of dissemination, with advice on what to do.

Upper Explosive Limit (UEL)

Maximum airborne concentration of a compound above which vapours will not ignite for lack of oxygen.

NB There are four annexes to this document. The files are pdf files.

Names of files:

Chapter26_Add.1_Evaporators.pdf "Intervention on gases and evaporators, card number F1.1, F1.2, F1.3"
Chapter26_Add.2_Floaters.pdf "Intervention on floaters, card number F2.1, F2.2"
Chapter26_Add.3_dissolvers.pdf "Intervention on dissolvers, card number F3"
Chapter26_Add.4_sinkers.pdf "Intervention on sinkers, card number F4"