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**Hazard Assessment of Floating
Chemicals after an Accident Spill at Sea**

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**HAZARD ASSESSMENT OF FLOATING CHEMICALS
AFTER AN ACCIDENTAL SPILL AT SEA**

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SUMMARY

The IMO-BCH (International Maritime Organization-Bulk Chemicals Subcommittee) have developed a classification system for hazard identification of compounds transported in bulk by sea designed to cover two situations. The first is for an accidental spill which is covered by the ship type allocation. The second is for the deliberate discharge of tank washings (slops). Within the IMO-BCH system, aquatic toxicity is assessed using data from acute toxicity tests preferably with sensitive marine organisms. The possibility of effects at lower concentrations on more sensitive species or life stages, or over a longer period, is considered in establishing the levels determining the toxicity classes.

When assessing hazard resulting from an accidental spill there is a requirement for both toxicity data and the environmental exposure concentration to the spilled product. At present, the latter is not formally considered in the IMO-BCH classification system. As the quantity of a product spilled will be a predominant factor in determining the affected volume of the sea after an accident, this factor is of particular importance in the ship type allocation procedure which considers the actual volume of compound which may be carried in one tank or one ship.

Environmental concentrations may be predicted with an environmental computer model called CHEMSPIL. It can be used to predict the exposure resulting from an accidental spill of a poorly water soluble, volatile and low density product. The CHEMSPIL model does not at present include an allowance for dispersion of the floating layer (e.g. droplet formation) caused by breaking waves; it has been suggested that under rough sea conditions compounds which normally would float can be held in dispersion as droplets until completely dissolved. Conversely products which float and have a high volatility will largely evaporate on spillage. These questions, and the matter of validation of the model under sea conditions, are being examined by others, especially by

the North Atlantic Treaty Organisation - Committee on the Challenges of Modern Society (NATO-CCMS).

The uncertainties that exist following accidental spill at sea are greater with respect to environmental concentration than as regards the toxicity of products. The existing CHEMSPIL model, which allows comparison between compounds under mild sea conditions, is only a first step in improving this aspect. The model could with advantage be developed to include the influence of dispersion and turbulence under rough sea (breaking wave) conditions on water concentrations.

The possibility of devising a laboratory test which would simulate an accidental spill situation has been considered. It is concluded that no simple test exists which would give a direct measurement of hazard. The development of such a test will be difficult.

In view of the importance of exposure in determining hazard, it is suggested that in its case by case consideration of products, the IMO-BCH could use the CHEMSPIL model to predict volumes of sea contaminated from spills of standard tank volumes, together with the normally available product data, to aid them in their task of allocating ship types.

A. INTRODUCTION

Large volumes of chemical products are shipped over the sea in bulk by tanker. To minimise the risk of significant environmental damage from their accidental or deliberate release (via tank washings) into the marine environment, chemicals transported in bulk by sea are regulated under Annex II of the Marine Pollution Convention (MARPOL 73/78). On the basis of a hazard profile defined by the Joint Group of Experts on the Scientific Aspects of Marine Pollution, working group on the Evaluation of the Hazard of Harmful Substances carried by ships (GESAMP-EHS), the Bulk Chemicals Subcommittee (BCH) of the Marine Environmental Protection Committee (MEPC) of the International Maritime Organisation (IMO) assigns a product to a pollution category and ship type with the objective of preventing pollution of the sea.

GESAMP-EHS assign aquatic toxicity ratings to products on the basis of acute toxicity data obtained according to internationally agreed guidelines. Such guidelines require that test species are exposed to constant, known concentrations. A number of the products that have to be considered are poorly water soluble, volatile, low density compounds or mixtures, here called floating compounds. Preparing and maintaining test solutions of such products requires carefully defined procedures. Since such procedures are not yet incorporated into internationally agreed guidelines, GESAMP-EHS has provided advice on maintenance of constant concentrations in the test system. Data produced under these defined conditions have in certain cases revealed lower LC_{50} values than had been anticipated and a few products, originally assessed prior to the mid seventies when no internationally agreed test guidelines had come into force, have had their aquatic toxicity rating upgraded.

Reliable LC_{50} values are needed to assign a toxicity rating. For the allocation of a ship type for the maritime transport of a chemical, the toxicity rating is only one parameter considered; the exposure expected after an accidental spill is the other important parameter. Although it can be argued that test concentrations should be maintained constant to obtain a reliable LC_{50} , under actual environmental conditions sufficiently high

concentrations may not exist long enough to produce adverse effects on marine organisms. A mathematical approach was proposed from industry (CHEMSPIL) in which the influence of the physico-chemical properties of a product were taken into account when estimating environmental concentrations resulting from an accidental spill. Although the principle of the approach was accepted, the IMO-BCH questioned whether it was relevant in all cases.

ECETOC (European Chemical Industry Ecology and Toxicology Centre) was asked to consider and advise on the scientific aspects of this matter. To get a better insight into the problem a one day workshop was organised at which interested parties could express their views (ECETOC, 1989). Subsequently, a Task Force was convened to review and advise on this matter. The Task Force received the following terms of reference:

1. to investigate the influence of physico-chemical properties on the fate of poorly soluble, low-density and highly volatile chemicals discharged into the sea and the effect on marine life;
2. if appropriate, to suggest modifications to procedures and supply appropriate supporting evidence to substantiate any changes.

The definitions of some of the most important terms and abbreviations used in this report are given in Appendix 1.

B. BACKGROUND

The Hazard Profile, as established by GESAMP-EHS (see Appendix 2), rates products on five properties of which one, Column B: Damage to Living Resources, is of particular importance to the present study. This aspect is rated according to the lethal concentration (LC_{50}) of the product to aquatic organisms (preferably a marine crustacean or fish). The rating system and the resulting impact on ship type allocation and pollution categorisation were designed to include appropriate safety factors to allow for variations in species susceptibility and for longer term effects. Water solubility and reactivity with sea water are two parameters considered during the aquatic toxicity test used in establishing the column B ratings of a product (Adema in ECETOC, 1989; IMO, 1989).

The Hazard Profile is used by IMO-BCH to establish a Pollution Category (which defines conditions for the discharge of tank washings) and Ship Type (which determines the likelihood of release in case of accident) for each product (see Appendix 2). To date, some 1800 products have been considered.

Use of a Hazard Profile which takes into account only the inherent toxicity of a product has been criticised because the exposure of marine organisms to a spilled chemical is not taken into account. The actual exposure in the marine environment will not only depend on the quantity of chemical released but also on the physico-chemical properties of a chemical. The exposure can, for example, be significantly reduced if it tends to evaporate from, rather than dissolve in sea water.

Wolff and Poels (1986) developed a model which permits a calculation of a predicted environmental concentration (PEC) resulting from an accidental spill. The model takes into account not only the quantity of chemical released but also the physico-chemical properties of the chemical. The PEC could be taken into account alongside toxicity in deriving Ship Types. In developing this approach it became clear that for one particular group of

products (i.e. those poorly water soluble, volatile products with a density lower than that of sea water), the potential exposure would be reduced sufficiently (Poels and Wolff, 1986) so that this factor should be given further consideration for the ship type allocation.

In Chapter C the influence of particular physico-chemical properties on the determination of acute toxicity are discussed. Practical guidance on exposure assessment after chemical discharges into the sea is given in Chapter D. Knowing the toxicity of a chemical and its predicted environmental concentration in the marine environment, a hazard assessment can then be performed. Some preliminary experiments which attempted to directly assess the hazard of floating compounds released into the marine environment are described in Chapter E. In Chapter F general recommendations are given for the hazard assessment of products transported in bulk by sea.

C. ASSESSMENT OF ACUTE AQUATIC TOXICITY

1. INTRODUCTION

Acute aquatic toxicity tests are used to determine the concentration of test substances which produce a defined deleterious effect on a group of test organisms during a short-term exposure under controlled conditions. Acute toxicity is usually expressed in terms of an EC_{50} value, that is the concentration of the substance in water which shows a defined effect in 50 % of the test organisms. The EC_{50} depends on the period of exposure and so is expressed as a time-dependent value, e.g. 96 hour EC_{50} . When the defined effect is lethality the term LC_{50} is used.

2. PRINCIPLE OF THE TEST METHOD

In determining a LC_{50} the concentration of the test substance to which the test species is exposed should remain constant. Testing at constant concentration is generally accepted by international guidelines (OECD, 1981). Some of these guidelines recommend, and others require, that the LC_{50} should be calculated on the basis of measured concentrations. The use of flow-through or renewal systems to keep concentrations constant during testing, in addition to keeping containers closed for highly volatile substances, has been common practice since about 1970.

Nevertheless, in the early days of aquatic toxicity testing, investigators calculated LC_{50} values on the basis of nominal concentrations, i.e. the concentration judged from the amount of substance added to the test system. This ignored the possibility that, on occasion, test substances dosed to water either do not completely dissolve or disappear quickly.

At the meetings preceding the International Conference on Marine Pollution in 1973 and at the first meetings of the GESAMP-EHS working group, the aquatic toxicity of a few substances may have been underestimated because

the above factors were not taken into account. Such ratings are at present being reviewed.

3. SPECIFIC FEATURES OF THE TEST PROCEDURE

3.1. Selection of Test species and Duration of Exposure

Tests with adult and sub-adult crustaceans or fishes exposed for a period of 48 to 96 h are the most common in aquatic toxicology. Many species are readily available and easy to handle and LC₅₀ tests with them have been standardised, validated (by ring tests) and shown to be reproducible. Many data produced using these species are available in the literature.

It has been claimed that such acute tests may allow an estimate of the long term lethal concentration of substances (Adema, 1985) where the asymptotic LC₅₀ is approached within 96 h (see Fig 1 line a) but not in cases illustrated by a toxicity curve as in Fig 1 line b.

The GESAMP-EHS working group is fully aware that other stages in the life cycle of aquatic organisms may be more sensitive than those which are usually the subject of acute toxicity testing. Chronic and sub-lethal effects may also manifest themselves after prolonged exposure to much lower concentrations than those which cause acute toxic effects. The effects observed at lower concentrations and longer exposure times may be more important for the ultimate effect on the marine ecosystem. The hazard profile system required by IMO simply calls for a means of ranking toxicity. The only type of data sufficiently widely available to permit this to be done with reasonable accuracy is that relating to acute toxicity tests. Nevertheless the working group when ranking chemicals based on acute toxicity data take into account the above considerations.

In the context of accidental spills and deliberate discharges, it was considered that if the 96 h LC₅₀ exceeded 1000 mg/l, it was unlikely that the chemical would be hazardous to marine organisms. Similarly,

any substance with a 96 h LC₅₀ less than 1 mg/l was considered to be sufficiently toxic to merit the strictest precautions to prevent it entering the sea. Between these, three further categories were introduced within the column B ratings (see Appendix 2 - Table A2-2).

3.2. Acute Toxicity Testing of Chemicals with Extreme Physico-Chemical Properties

The column B ratings are based on results of aquatic toxicity tests and do not take into consideration the problems which may arise as a result of the physico-chemical properties of the test chemical. Testing of chemicals which have a low water solubility or which may volatilise from the solution may lead to inaccurate estimates of their toxicity. The GESAMP-EHS working group is currently discussing these difficulties. The sections below consider some features of the problems.

- 3.2.1. Influence of Solubility in Water. For compounds with a low water solubility care should be taken that the dosed amounts are actually dissolved in (sea)water before the animals are introduced in the test system. This may require some time. When small amounts are introduced in the test system visual control of solubilisation is not adequate and chemical analysis is necessary. In many cases aids are necessary to improve the dissolution e.g. mechanical means and/or use of co-solvents. The use of such aids should be limited to an improvement of the handling and dispersion of the test substance but should not be used to increase its water solubility or, for example, produce an emulsion. Much evidence is found in the older literature that no consideration was given to the solubility of the test substance. LC₅₀ estimates were often based on nominal concentrations which were in reality higher than the solubility limits.

For LC₅₀ values based on measured concentrations, relations have been found between the aqueous solubility and the aquatic toxicity of non-dissociated substances. Könemann (1981) described a quantitative structure-activity relation (QSAR) for fish (Poecilia reticulata) between the LC₅₀ in µM/l and the octanol/water partition coefficient

(Pow) which itself is in many cases inversely related to the water solubility:

$$\log \frac{1}{LC_{50}} = 0.871 \log Pow - 4.87$$

For crustaceans (Daphnia magna) a similar QSAR was derived by Hermens et al. (1984):

$$\log \frac{1}{EC_{50}} = 0.91 \log Pow - 4.72$$

The results in Table 1 for the aquatic toxicity of alcohols to fathead minnows show clearly a direct relationship between the LC_{50} and the water solubility and an inverse correlation with the octanol/water coefficient (Veith et al., 1983). The consequence of the above findings for the column B ratings of alcohols is a gradual increase in toxicity with decreasing solubility (or increasing carbon numbers) up to the point where the solubility is so low that there are not enough molecules in solution to kill the fish within the exposure time; in the case of 1-tridecanol the result being a column B rating of '0'. Such "breakpoints" also occur in other homologous series of compounds.

Another example of the relationship between aqueous solubility and toxicity is given in Table 2.

As predicted by the QSAR of Hermens (1984), hexane is more toxic than benzene. In general the less soluble, the more toxic the substances were within the investigated limits.

3.2.2. Influence of Vapour Pressure. Similar problems may arise when testing volatile substances. Inaccurate LC_{50} values are obtained when the calculations are based on nominal concentrations. When performing a

test, concentrations should be kept constant and determined. Loss by volatilisation should be minimised and adequate analytical procedures should be used. Testing in closed systems is recommended. Although the measured LC₅₀ values are adequate for ranking substances according to their toxicity (B ratings) a further hazard assessment should consider the actual concentrations and residence times under environmental conditions when the chemicals are released in the aquatic environment.

3.2.3 Testing of Mixtures. Many industrial substances are not single compounds. When mixtures are of closely related chemicals which are readily water soluble they can be tested similarly to pure compounds. On many occasions mixtures are produced with substances with diverse physico-chemical properties (e.g. formulations). Such mixtures are far more difficult to test and evaluate meaningfully.

Considering the variation in solubility of the different components, the GESAMP-EHS working group published advice on how to prepare test solutions of such mixtures in Reports and Studies No 35 (IMO, 1989). The advice is based on the use of "*water-accommodated fractions*" (WAF) prepared by the shake-flask method (Girling, 1989). Except for the preparation of the test solutions, the principles of the test are the same as those for other substances.

D. ASSESSMENT OF ENVIRONMENTAL CONCENTRATIONS

1. PARAMETERS DETERMINING ENVIRONMENTAL CONCENTRATIONS

An estimation of the concentration in the marine environment after a spillage depends on a knowledge of the main physical, chemical and biological processes that operate under these conditions. These processes will depend not only on the properties of the spilled chemical but also on the properties of the seawater and other site specific environmental parameters.

For poorly water soluble, highly volatile chemicals with a lower density than seawater the main processes which have to be considered after a spillage are listed in Table 3. The inherent properties of the chemicals of particular interest in this report are given in more detail in Table 4. Environmental and local parameters which will also determine the environmental concentration of a spilled chemical are listed in Table 5.

The main processes which influence the behaviour and fate of chemicals after an accidental spill are discussed below.

1.1 Spreading on the Water Surface

The surface area of a spilled liquid on the sea surface as a function of time can be described by the Fay model developed for oil layers which considers three consecutive phases (CONCAWE, 1983).

Initially spreading of the spilled layer is determined by gravity forces which are only resisted by the inertia of the compound. In a second phase gravity forces are resisted by the viscous retardation of the chemical and in a third phase the surface tension forces are resisted by the viscous forces in the sea water. The first two phases of the spreading process occur relatively rapidly compared to the third one.

The spreading times and the maximum extent of spreading depend on the spilled volume.

The model requires a knowledge of the density of the chemical and sea water, the spilled volume, the viscosity of the seawater and the spreading coefficient, defined as the difference between the air/water surface tension and the sum of the air/chemical surface tension and the chemical/water interfacial tension (CONCAWE, 1983). The spreading coefficient is only relevant for the third phase of the spill. A negative spreading coefficient is an indication that there will be break up of the spilled layer. The spreading coefficient has been determined for oils and ranges from 13 to 26 mN/m (CONCAWE, 1981). The spreading coefficients determined for chemicals range from -13 mN/m for allyl chloride to 46 mN/m for butyl alcohol (Dodge et al., 1983).

1.2 Evaporation

The evaporation process can be divided into the evaporation from the floating layer and the evaporation from the water after dissolution. The rate of evaporation from the floating layer can be estimated using a model developed by Mackay (CONCAWE, 1983). This model is applicable to crude oil and similar mixtures. For highly volatile compounds heat transport can become rate determining as rapid evaporation will have a cooling effect.

Mathematical models were developed for the evaporation from the water phase (Mackay and Yeun, 1983; Mackay, 1985, 1988; Wolff and van der Heijde, 1982). Both models (i.e. those of Mackay and Wolff) are based on the two resistances model by Lewis and Whitmann (1924) and Liss and Slater (1974). The models, which were experimentally validated, require a knowledge of the diffusion coefficients in air and water and the Henry constant as product data, and water temperature, water depth and wind speed as environmental parameters. Diffusion coefficients can be calculated from molecular data e.g. the molecular volume (Hayduk and Laudie, 1974; Tucker and Nelken, 1982).

The fate of the evaporated chemicals is outside the scope of this report. It is, however, likely that they will in most cases be phototransformed in the troposphere mainly by reaction with OH-radicals (Atkinson, 1986).

1.3 Dissolution

Dissolution of a spilled chemical will mainly occur in the contact area between the liquid chemical and seawater. The boundary layer model of Lewis and Whitman (1924) can again be used to describe the dissolution rate which depends on the diffusion coefficient in water, the conceptual thicknesses of the boundary layers and the water solubility of the chemical. The dissolution is enhanced by turbulence and in general by any enlargement of the contact area between the liquid chemical and the water e.g. by formation of small droplets (Schuurmans et al., 1979) or by spreading on the water surface over a larger area. The presence of an organic water surface microlayer as well as variations of the water temperature also influence the dissolution process. For the hydrophobic chemicals considered here the influence of ionic components of the seawater will not increase the solubility.

1.4 Dilution and Transport in Water

The dissolved chemical will be diluted in the seawater by molecular diffusion and water turbulence (eddy diffusion). The dilution caused by molecular diffusion is influenced by the temperature and is slow compared to the eddy diffusion.

For the open ocean the lateral dispersion is described by an empirical formula derived by Fischer et al. (1979). In addition a volume of seawater containing the dissolved chemical can be transported as such by advection (horizontal transport) and convection (vertical transport). During advective and convective transport dilution also occurs.