Technical Report

No 39

Hazard Assessment of Floating Chemcials after an Accident Spill at Sea

July 1990

ISSN-0773-8072-39

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Brussels, 10 July 1990

ECETOC Technical Report No 39

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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 LC_{50} 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 LC_{50} 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 LC_{50} exceeded 1000 mg/l, it was unlikely that the chemical would be hazardous to marine organisms. Similarly, any substance with a 96 h LC_{50} 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. LC_{50} estimates were often based on nominal concentrations which were in reality higher than the solubility limits.

For LC_{50} 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 LC_{50} 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 LC_{50} 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.

1.5 Droplet Formation and Coalescence

The process of droplet formation depends on the type of accidental spillage and on the sea state (turbulence, waves, swirls). This process is enhanced with increasing density and decreasing viscosity of the chemical, decreasing floating layer thickness and interfacial tension and increasing roughness of the sea (breaking waves). The diameter of the dispersed droplet will be determined by the degree of turbulence of the sea and the viscosity of the dispersed material (Schuurmans et al., 1979; Lagisetty et al., 1986). As pointed out by Lange (1989) small droplets could be suspended in a waterbody for a sufficiently long time to allow all the material to dissolve. Resurfacing of the droplets is assumed not to occur when the rising velocity is less than 0.025 m/s (Schuurmans et al., 1979). The maximum droplet diameter which corresponds to this criterion depends on the difference between the density of seawater and the chemical (e.g. 0.15 mm diameter for a density difference of 200 kg/m^3 to 0.3 mm diameter for a density difference of 50 kg/m^3). Although such small droplets are only formed by a certain energy input, spill and weather conditions may well occur in practise at which such small sized droplets could be formed (Lange, 1989).

Small sized suspended droplets can coalesce. This depends on the physico-chemical properties of the substance and the constancy of the energy input. Emulsions are generally more unstable in seawater than in freshwater. For example even under the influence of a high energy input, turpentine formed only unstable emulsions in seawater which coalesced within a few seconds. The presence of surfactants enhanced the emulsification (Schuurmans et al., 1979).

1.6 Sorption Processes

The processes by which chemicals are associated with the solid phase in microlayers and suspended matter are often complex and not fully understood. They include truly surface processes (adsorption) as well as other forms of association.

Spilled chemicals may be sorbed on the organic microlayer which is present at the sea/atmosphere interface with a variable thickness of about 100 µm. This layer consists mostly of surface active organic compounds such as fatty acids, alcohols and lipids as well as proteinaceous material. It also contains substantial quantities of microorganisms, fish eggs and particulate organic matter (Hardy, 1982). Trace metals can be accumulated by complex formation in the organic microlayer.

The sorption process of organic compounds in such microlayers is well known and was recently reviewed (Valsaraj, 1988). This sorption process is more relevant for the environmental behaviour of highly diluted, non-polar and low volatile chemicals.

For the compounds under consideration here, adsorption may occur on suspended matter. In such cases the octanol/water partition coefficient of the chemical as well as the organic carbon content of the suspended matter can be used to estimate the adsorption potential on suspended matter (Kenaga and Goring, 1980; Karickoff, 1981). As only minor quantities of suspended matter are present in the sea these processes are only of secondary importance.

1.7 Biodegradation, Hydrolysis, Photodegradation

Biodegradation is one of the most efficient degradation pathways in the aquatic environment. It depends on the amount of microbial biomass and nutrients in the sea and often requires a period of adaptation. It can be assumed that biodegradation processes will normally be slow in comparison to the physico-chemical processes of dilution and evaporation for the chemicals under consideration.

In the accidental spill situation hydrolysis can only influence significantly the behaviour and fate of those compounds which react rapidly with water (e.g. some isocyanates or easily hydrolysable esters). For such reactive compounds a case by case evaluation is necessary.

Other abiotic reactions such as phototransformation reactions are too slow for many of the chemicals under consideration which have no, or only weak, absorption in the wavelength range of sunlight.

1.8 Other Parameters

Rain and snow will decrease the net loss by evaporation by washing out the evaporated chemical from the gas phase. If the sea is partly covered by ice the evaporation will be increased when the spill occurs on the ice and will be decreased when the liquid is trapped under the ice. Such phenomena are not relevant for a general classification.

2. *PRACTICAL APPROACH FOR PREDICTION OF ENVIRONMENTAL CONCENTRATIONS AFTER AN ACCIDENTAL SPILL.*

Each of the processes mentioned above proceeds simultaneously and some are mutually competitive. Therefore mathematical modelling is necessary to estimate the resulting exposure concentrations. Such model calculations use variable environmental parameters, spill parameters and the physico-chemical properties of the spilled chemical. For the first two types of parameter realistic values should be chosen (e.g. volume of the tanks in a chemical tanker). When these parameters are fixed only the inherent physico-chemical data of the chemical will influence the final concentration estimate. The results of such a model calculation can be used to compare the behaviour and fate of different chemicals after an accidental spill at sea. Wolff and Poels (1986) developed the CHEMSPIL model which is discussed below. Other models, however, also exist especially in Canada and the USA and are reviewed by the NATO-CCMS (1989) initiative.

2.1. Description of the Model

The CHEMSPIL model calculates the concentration of the dissolved chemical as a function of place and time. This is expressed as the area of the sea where concentrations are above a given limit, e.g. LC_{50} or 0.1 x

LC_{50}. Appendix 3 shows some practical examples of the use of the CHEMSPIL model.

The following processes are considered in the CHEMSPIL model:

- Dissolution, dilution (dispersion of the dissolved chemical). The model considers the dissolution from the surface layer of the spread chemical. The calculations are based on the boundary layer model of Lewis and Whitmann (1924). The mass flux, dependent on the thickness of the boundary layer, increases with the wind speed.

  For lateral dispersion of the dissolved chemical a formula given by Fischer et al. (1979) is implemented in the programme. For the "dispersion factor" α an exact value cannot be calculated and an average value of 0.7×10^{-4} $m^{2/3}/s$, derived from experimental data, is recommended as a default value. For the vertical dispersion coefficient an average observed value of 0.3×10^{-2} m^2/s is recommended (Wolff and Poels, 1986).

- Spreading, evaporation from the surface layer and from water. The spreading model of Fay (CONCAWE, 1983) is implemented in the CHEMSPIL model. For the spreading coefficient a default value of 25 mN/m, an average value experimentally found for oils, is recommended if no other data are available.

  The model of Mackay (CONCAWE, 1983) is used for the evaporation from the organic surface layer which requires the input of a boiling range. When dealing with pure compounds the boiling range is considered to be from the boiling point to the boiling point + $1^{o}C$.

  The evaporation from water is simulated in the CHEMSPIL model by the programme VRDAMP from Wolff and van der Heijde (1982). It seems from the literature (Mackay and Yeun, 1983) that for wind speeds above 10 m/s, measured at a height of 10 m, the VRDAMP model overestimates the mass transfer coefficient.

The following processes are not considered in the CHEMSPIL model:

- Dispersion of the organic layer. Natural dispersion caused by breaking waves is not included in the model because at present time no formula is available to describe this process.

- Transport processes. Advective and convective transport processes are not included in the model. These processes depend strongly on the specific environmental situation. They are assumed to cause more a displacement than an alteration of the contaminated area.

- Sorption and degradation processes. These processes are not included in the programme because they are assumed not to influence the behaviour of the chemicals under consideration substantially during the accidental spill situation.

- Heat transport. Decrease in evaporation caused by limited heat transport is not included in the programme. It is assumed to be relevant only in special cases.

2.2. Environmental Relevance

In principle the CHEMSPIL model can be used to compare the fate of substances as well as to predict their environmental concentrations after a spill situation. This is shown in Appendix 3 where the model is used for an accidental spill situation of three chemicals (aniline, benzene, hexane) of similar toxicity to fish but with different physico-chemical properties.

Whether the CHEMSPIL model describes a real situation with appropriate parameters has to be considered. If so consideration must be given to whether in realistic situations large deviation from the predicted concentrations could occur.

It would be reasonable to assume that for relatively calm weather conditions (absence of breaking waves) the CHEMSPIL model will provide a reasonable estimation of the environmental concentration after an accidental spill. To validate the accuracy of the predicted exposure concentrations it would be necessary to perform field experiments after an accidental or deliberate spill situation. At present proposals for a validation are being considered by NATO-CCMS (1989).

The CHEMSPIL model has certain limitations. The occurrence of breaking waves, strong currents and swirls can cause an increase of "natural dispersion" as well as advection and convection. Natural dispersion in general would be followed by an increase of the contact area between the floating layer and both the water and the air and it can be assumed that evaporation, dissolution and also dispersion processes would be enhanced. The formation of small emulsified droplets during rough weather, which would be followed by a large increase of dissolved compound, is still a hypothesis which has to be proven by experiment, although Lange (in ECETOC, 1989) suggests the possibility of such phenomena.

In coastal areas deviations in the dispersion behaviour could occur because the formula for lateral dispersion used in the model is only valid for open sea areas. Vertical dispersion would be modified in shallow waters.

2.3. Application of the CHEMSPIL Program to Mixtures.

In general the CHEMSPIL programme was not developed for mixtures of compounds, although one of the subroutines is also applicable to mixtures (the Mackay approach on the evaporation from the organic layer).

For mixtures of compounds which are closely related with respect to their physico-chemical properties and toxicity, mean values which reflect the composition of the mixture may give reasonable estimates. Nevertheless it is preferable with mixtures to calculate the environmental concentration of each selected substance separately using its molar fraction in the mixture. This approach is also recommended for impurities which are of significance with respect to their quantity or toxicity.

2.4. Conclusions and Recommendations

The CHEMSPIL model allows the calculation of the contaminated sea volume as a function of the spill volume and physico-chemical properties of the spilled product. It can be used to make valid comparisons between products under mild sea conditions and the absolute concentrations predicted to be realistic under open sea conditions.

The model could with advantage be validated by direct experiment under mild open sea conditions. It could also be extended to include the influence of turbulence under rough sea conditions on dispersion and the influence of near shore conditions. These aspects would need study under simulated conditions as well as eventual validation at sea. It is understood that studies along these lines are being considered by an NATO-CCMS initiative.

E. SIMULATION EXPERIMENTS FOR DIRECT HAZARD ASSESSMENT OF CHEMICALS ACCIDENTALLY SPILLED IN THE MARINE ENVIRONMENT

It was thought that instead of standard acute toxicity tests other tests could be devised which would directly estimate the toxicity of a chemical under real environmental conditions which would occur during an accidental spill. Independently three laboratories performed preliminary toxicity tests in which no attempt was made to maintain a constant concentration in the aqueous solution (ECETOC, 1989).

The Exxon procedure used a dispersion system designed to simulate an operational release. The test substances were complex mixtures containing components covering a range of volatilities and solubilities. Open 19 litre test chambers were loaded with excess test substance ranging from 5 to 5,000 mg/l and the contents continuously stirred. This procedure encourages volatile components to escape. Thus the test substance will change in composition during the test. The test species used was the fathead minnow (Pimephales promelas) with ten animals in each of two replicate test chambers at each test concentration. The mortality was recorded and a 96 h $LC(I)_{50}$ value (Lloyd and Tooby, 1979) calculated from quantities of test substance initially added (Table 6). In those cases where the water solubility was exceeded the animals were probably exposed to both soluble and dispersed fractions.

The ICI test assessed the toxicity of pentane in open test vessels. The test solutions were prepared by adding the required volume of test substance to 10 litres of seawater which was then shaken in a sealed glass jar for 15 minutes on a mechanical shaker. The procedure was repeated for each test concentration. When all were prepared the contents of the jars were added to the test vessels containing 20 litres of dilution water. Twenty test animals (the brown shrimp, Crangon crangon) were placed into each test vessel and the mortalities recorded. The solutions were not renewed during the 96h period of the test. The results are given in Table 6. Due to the high volatility of pentane, the nominal concentrations were never achieved even at the start of the test, and there was a continual loss over the whole test period to levels below the analytical detection limit at the end of the test. Although the results are useful, no LC_{50} value can be derived from this study as clearly the concentrations were not maintained and a mean of the analytical values would be misleading with such a high rate of loss. The only conclusion which can be derived from these experiments is that the 96h LC_{50} must be below 3.5 mg/l.

The TNO test compared the results from four different test methods, the test vessels being: closed (stoppered Erlenmeyer flasks); covered (in glass beakers with watch glasses); or open (uncovered glass beakers) with and without renewal. The test solutions were prepared by pipetting the required amount of test substance (either toluene or hexane) into 2.2 litres of natural seawater and stirring for 4 hours in a glass stoppered Erlenmeyer flask. The water phase was then drawn off into the test vessels and the test animals (the crustacean, Chaetogammarus marinus) were added, 10 animals in approximately 1 litre of solution. There was no undissolved compound visible in the test solutions. The test duration was 96 hours and the solutions were renewed daily except for the no renewal test.

The results obtained are given in Table 6. The LC_{50} results for toluene, based on nominal concentrations are the same (18 mg/l) for all time periods and for all test methods, even for the no renewal test where there was only 0.6% of the nominal concentration present at the end of the test. A possible explanation for this finding would be that toluene exerts its acute lethal action over a short period of time (<24 hours) after which no further deaths occur. The compound is present, even in the open beakers, for sufficient time and at a sufficient concentration to cause maximum mortality before being lost from solution. When the LC_{50} value is determined using the average measured concentration the open method shows a significantly lower LC_{50} value than the other methods (Table 6). Hexane shows a slightly different response; the 24h LC_{50} values are similar for all test methods. The estimated 96h values for the renewal methods are lower, but for the "no renewal" the value remains approximately the same. In the latter case hexane has been lost before it has reached the limit of its acute lethal effect and thus the overall toxic effect is reduced.

From the work of ICI and TNO it can be concluded that chemicals with low solubility and low density are lost from solution under "open" laboratory test conditions. Even under "open" and "no renewal" conditions the effects of some chemicals (e.g. toluene) with extreme physico-chemical properties may not be reduced. It should be noted that the results obtained with toluene, hexane and pentane would not alter their present GESAMP rating.

In the Exxon studies complex mixtures were used as test substances. No chemical analysis was carried out and the rate of loss of any of the components could therefore not be assessed. Test results with such a system may well depend on test design details, the initial amounts of chemical added or other arbitrarily chosen variables.

The open sea is a dynamic system and therefore no single standardised and scientifically valid test can be devised which would provide the information required for a hazard assessment of a chemical released under marine conditions. The degree to which marine release conditions are simulated with the above systems is questionable and in particular results from such tests, where appreciable losses occur, should not be expressed in terms of LC_{50} or even $L(I)C_{50}$.

F. HAZARD ASSESSMENT OF CHEMICALS ACCIDENTALLY SPILLED AT SEA

Hazard is a qualitative term expressing the potential of a product to cause harm under particular conditions of exposure (Richardson, 1988). An environmental hazard assessment therefore involves the consideration of the ability of a compound to harm the environment and the exposure of the environment to that compound. It is normally performed by comparing the predicted environmental concentration of a compound with a measure of the toxicity of that compound, often an LC_{50} or a 'no observed effect' concentration.

The aquatic toxicity of floating compounds accidentally spilled at sea can be satisfactorily assessed provided certain test requirements are met. Direct assessment of hazard by laboratory experiment has also been investigated and it was concluded that this was not reliable.

It has been shown that the CHEMSPIL model can rank different chemicals according to the exposure concentrations expected after an accidental spill under calm sea conditions. Thus, a comparative hazard assessment can be made by calculating the maximum volumes of sea contaminated above the LC_{50} value for spills of the same volume of different compounds. This has been done for three compounds of similar toxicity but different physico-chemical properties: aniline, benzene and hexane. The calculations show that for a spill volume of 60 m^3 the volumes of sea contaminated were 3.9×10^6, 6.7×10^4, and 0 m^3 respectively.

A further comparison between aniline and benzene has been made by using the CHEMSPIL model to predict the volume of sea contaminated by different spill volumes of benzene and hence deriving the volume of benzene that would contaminate the same volume of sea as 60 m^3 of aniline. From these simulations, it has been shown that 4400 m^3 of benzene would contaminate the same volume of sea as 60 m^3 of aniline. Such comparisons could be of value in establishing both the volumes and ship types in which products could acceptably be transported.

The value of the CHEMSPIL model for hazard assessment could be increased in two aspects. To predict absolute concentrations, rather than to provide only comparative data, requires validation of the model by investigating a (deliberate) release at sea. To allow comparative and absolute predictions under rougher sea conditions, the effect of breaking waves on the distribution of a floating compound must be added to the model. This may well require experimentation under deliberate but controlled conditions followed by validation in a real situation. It is understood that studies along these lines are being considered by a NATO-CCMS (1989) initiative. This initiative is to be welcomed and supported.

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TABLE 1
ACUTE TOXICITY OF ALCOHOLS TO FATHEAD MINNOW

Chemical	96h LC_{50} (mg/l)	S (mg/l)	log Pow	LC_{50}/S	Column B rating (GESAMP)
Methanol	28100	+	- 0.66	-	0
2-ethanol	14200	+	- 0.16	-	0
2-propanol	10400	+	0.14	-	0
1-butanol	1730	74700	0.88	0.023	0
1-hexanol	97.5	6270	2.03	0.016	1
1-octanol	13.5	587	3.03	0.023	2
1-nonanol	5.7	158	3.53	0.036	2
1-decanol	2.4	34	4.03	0.070	3
1-undecanol	1.0	8.5	4.53	0.122	3
1-dodecanol	1.0	1.9	5.00	0.532	3/4
1-tridecanol	*	0.33	5.51	>1.0	0

* no fish mortality in saturated solution (from Veith et al., 1983)

S = water solubility

Pow = octanol/water partition coefficient

TABLE 2
ACUTE TOXICITY OF HYDROCARBONS

Compound	Mol. W	S (mg/l)	Acute toxicity (mg/l)		
			48h LC_{50} 1) D. magna	96h LC_{50} 2) M. bahia	predicted QSAR 3)
n-hexane	86	~ 10	3.9	2.4	4.8
cyclohexane	84	~ 55	3.8	3.1	11
benzene	78	~ 1800	36	22	71

1) Bobra et al. (1983)
2) Adema (pers. comm.)
3) Hermens (1984)

TABLE 3

PROCESSES INFLUENCING THE BEHAVIOUR OF CHEMICALS AFTER AN ACCIDENTAL SPILL

Process	Inherent Property of the Chemical	Environmental Parameter
dissolution	water solubility	wind speed, turbulence
dilution in water by diffusion and turbulence	diffusion coefficient	turbulence
transport in water by advection (horizontal) and convection (vertical)		currents, swirls, temperature gradients
spreading	density, interfacial tension, surface tension	seawater density, viscosity, surface tension
dispersion of the floating layer and small droplet formation	interfacial tension, viscosity, density	wind speed, turbulence, wave intensity
evaporation from the floating layer	vapour pressure	wind speed, turbulence, temperature
evaporation from aqueous solution	Henry constant (solubility and vapour pressure)	wind speed, turbulence, temperature
absorption	octanol-water partition coefficient	organic microlayer
adsorption	adsorption coefficient	amount of suspended solids and their organic C content
biodegradation	biodegradability	microbial biomass, nutrients, temperature
hydrolysis	reactivity towards water	temperature, pH
phototransformation	photoreactivity, light absorption	light intensity, wavelength

TABLE 4

INHERENT PROPERTIES OF THE CHEMICALS

	Unit
Inherent physical chemical properties	
water solubility (S)	kg/m3
vapour pressure (P)	Pa
Henry constant (P/S in molar units)	Pa.m3/mole
boiling point	°C
melting point	°C
molecular weight	kg/mole
density	kg/m3
spreading coefficient	N/m
octanol/water partition coefficient	
adsorption coefficient	
diffusion coefficient in water	m2/s
diffusion coefficient in air	m2/s
surface tension (air/chemical)	N/m
interfacial tension (chemical/water)	N/m
Degradation pathways	
abiotic reactions (hydrolysis, photodegradation)	(rate constant)
biodegradation	(rate constant)

TABLE 5

VARIABLE PARAMETERS IN A SPILL SITUATION

Property	Unit
Variable of the release	
quantity of the spilled chemical	kg
mode of the release of the spilled chemical into the sea (gradual or instantaneous; on surface or below surface, etc)	
Properties of the receiving water	
dynamic viscosity	Pa/s
density	kg/m3
surface tension	N/m
Environmental parameters	
water depth	m
water temperature	°C
air temperature	°C
wind speed	m.s-1
turbulence, swirls and currents	
organic surface microlayers	
presence of biomass	
other meteorological conditions (rain, snow, ice, light intensity)	

TABLE 6

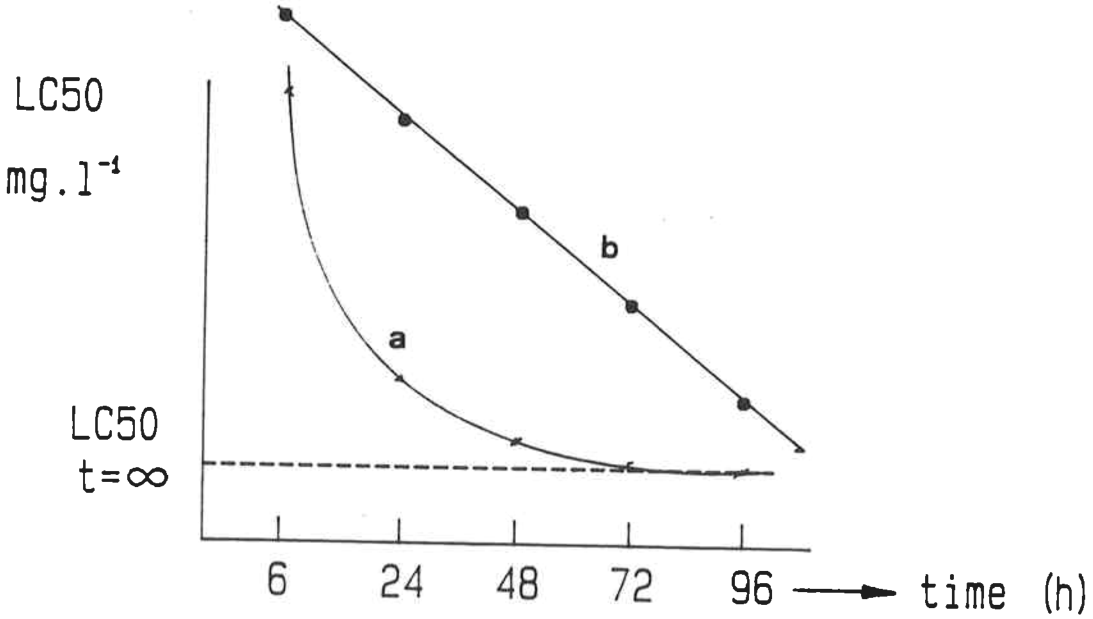
RESULTS SIMULATION TESTS

Material/method	Lab.	LC_{50} values (mg/l)				Chemical analysis (% nominal) exposure time (hours)				Reference
		based on nominals			measured*					
		24h	48h	96h	96h	0h	24h	48h	96h	
Aromatic solvent - dispersion	Exxon			40.6						ECETOC (1989)
Stoddard solvent - dispersion	Exxon			600						
Hydrotreated light distillate - dispersion	Exxon			2,200						
Paraffin solvent - dispersion	Exxon			>5,000						
Hydrotreated heavy naphtha - dispersion	Exxon			>5,000						
Pentane - no renewal - open	ICI		7.0	7.0	1.0	29.0		10.2	<3.0	ECETOC (1989)
Toluene - no renewal - open	TNO	18		18	9.7	107			0.6	
Toluene - renewal - open	TNO	(20)		18	11.8	100	31			
Toluene - renewal - covered	TNO	18		18	13.4	96	53			ECETOC (1989)
Toluene - renewal - closed	TNO	18		18	16.0	96	82			Adema
Hexane - no renewal - open	TNO	11		10	1.9	38			0.25	(pers. comm.)
Hexane - renewal - open	TNO	12		5	0.33	10	3.1			
Hexane - renewal - covered	TNO	10		6	0.75	17	8.1			
Hexane - renewal - closed	TNO	10		6	0.81	15	12			

* Based on mean values

FIGURE 1

LC_{50} IN FUNCTION OF EXPOSURE DURATION



APPENDICES

APPENDIX 1

DEFINITIONS AND ABBREVIATIONS

- *BCH* - IMO - Bulk Chemicals Subcommittee of the International Maritime Organisation.

- *CONCAWE* - Conservation of Clean Air and Water in Europe (Oil Companies Study Group, Brussels).

- EC_{50} - Median effective concentration. The concentration of material in water to which test organisms are exposed that is estimated to be effective in producing some defined response in 50 % of the test organisms. The EC_{50} is usually expressed as a time-dependent value (e.g. 24-h or 96-h EC_{50}). The response elicited from the test organisms as a result of exposure to the test material must be clearly defined. For example, test organisms may be immobilised or undergo physiological or behavioural changes.

- *ECETOC* - European Chemical Industry Ecology and Toxicology Centre.

- *EHS* - IMO - Working Group on Evaluation of Harmful Substances.

- *GESAMP* - IMO - Joint Group of Experts on the Scientific Aspects of Marine Pollution.

- *IMO* - International Maritime Organisation.

- LC_{50} - Median lethal concentration. An EC_{50} where the defined response is death.

- $LC(I)_{50}$ - An LC_{50} based on initial nominal concentrations of the test solutions.

- *MARPOL* - Marine Pollution Convention.

APPENDIX 2

GENERAL PROCEDURES TO ESTABLISH GESAMP HAZARD PROFILES

An example of a hazard profile is shown in Table A2-1, and the ratings it lists are explained in Table A2-2. So far about 1800 substances have been rated, some incompletely (IMCO, 1981; IMO, 1989).

TABLE A2-1
HAZARD PROFILE (example)

	Bioaccumulation and tainting	Damage to living resources	Hazard to human health		Reduction of amenities	
			Oral intake	Skin contact and inhalation		
Substances	A	B	C	D	E	Remarks
Acetone	0	0	1	I	X	Tested for tainting
Benzene	0	2	1	II	XXX	Human carcinogen; Haemotoxic; Tested for tainting
Ethylene glycol	0	0	1	II	XX	Teratogen
Toluene	0	2	1	II	XX	Neurotoxic; Ototoxic; Tested for tainting
Xylene (mixed isomers)	0	2	1	I	X	Tested for tainting

(for a description of the coding used in the above table refer to Table A2-2)

TABLE A2-2

Hazard Profile System

Column A - Bioaccumulation and Tainting

+	Bioaccumulated to significant extent and known to produce a hazard to aquatic life or human health
Z	Bioaccumulated with attendant risk to aquatic organisms or human health, however with short retention of the order of one week or less
T	Liable to produce tainting of seafood
0	No evidence to support one of the above ratings (+, Z, T)

Column B - Damage to living resources

Ratings		96 hr LC_{50}
4	Highly toxic	less than 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	greater than 1000 mg/l
D	Substance likely to blanket the sea-bed	
BOD	Substance with oxygen demand	

Column C - Hazard to human health by oral intake

Ratings		LD_{50} (laboratory mammal)
4	Highly hazardous	less than 5 mg/kg
3	Moderately hazardous	5-50 mg/kg
2	Slightly hazardous	50-500 mg/kg
1	Practically non-hazardous	500-5000 mg/kg
0	Non-hazardous	greater than 5000 mg/kg

Column D - Hazard to human health by skin and eye contact or inhalation

II	Hazardous (severe irritation, strong sensitiser, lung injury, percutaneous toxicity, carcinogenic or other specific long-term adverse health effect)
I	Slightly hazardous (mild irritation, weak sensitizer)
0	Non-hazardous (non-irritant, not a sensitizer)

Column E - Reduction of amenities

XXX	Highly objectionable because of persistency, smell or poisonous or irritant characteristics; as a result contaminated beaches liable to be closed; also used when there is clear evidence that the substance is a human carcinogen or that the substance has the potential to produce other serious specific long-term adverse health effects in humans.
XX	Moderately objectionable because of the above characteristics, but short-term effects leading only to temporary interference with use of beaches; also used when there is credible scientific evidence that the substance is an animal carcinogen but where there is no clear evidence to indicate that the material has caused cancer in humans, or when there is evidence from laboratory studies that the substance could have the potential to produce other serious specific long-term adverse health effects.
X	Slightly objectionable, non-interference with use of beaches
0	No problem

Ratings in brackets, ( ), indicate insufficient data available to the GESAMP experts on specific substances, hence extrapolation was required.

N	Not applicable (e.g. if gases)
-	Indicates data were not available to the GESAMP Working Group

Note: The descriptive terms such as highly toxic, non-hazardous, etc., were used by the original panel for the purposes of the 1973 International Conference on Marine Pollution. They have no particular significance in terms of hazard posed outside the particular circumstances addressed by that Conference and IMO Sub-Committees, i.e. marine pollution as a consequence of discharges or spillages from ships.

The hazard profiles are used by IMO to indicate the pollution category of the substances (Table A2-3), and for ship type allocation (Table A2-4). The EHS Working Group produces the hazard profiles, but has little or no say in how they are used.

TABLE A2-3
IMO Pollution Categories
defined according to the Hazard Profile ranking

Annex II pollution category	Hazard profile			
	A	B	C	E
category A	+	-	-	-
	-	4	-	-
	T	3	-	-
	Z	3	-	XXX
category B	T	-	-	-
	Z	-	-	-
	-	3	-	-
	-	2	-	XXX
category C	-	2	-	-
	-	1	4	XX
	-	1	3	XX
category D	-	1	-	-
	-	-	4	-
	-	-	3	X
	-	-	-	XXX
	-	-	-	XX
	-	D/BOD	-	-

TABLE A2-4
IMO Ship Type Allocation
resulting from the Pollution Category ranking of a chemical

Ship type	Bioaccumulation and tainting A	Damage to living resources B	Reduction of amenities E
1	+	4	
	+		XXX
	T	4	
2	+		
	Z	4	
	Z	3	
	Z		XXX
	T		
	0	4	
	0	3	XXX
3	All other substances falling under pollution categories A, B and C.		

DETAILS ON COLUMN RATINGS

The basis for the column B ratings is given in the following paragraph of Reports and Studies no. 17/35.

1. Basis for the Ratings

In order to rank the hazard posed to living resources, the most practical solution available was considered to be the use of acute toxicity test data. Wherever possible, 96h LC_{50} data relating to marine species are used and, wherever possible, the Working Groups use data relating to adult or juvenile stages of organisms representing the middle to upper levels of an aquatic food chain, e.g. crustacea or fish. Where data are not available for marine species but are available for freshwater species these may be used after due consideration of the possible effect on toxicity of the different water medium. Where data are available for several species, generally the figure which indicates the greater degree of hazard is used. Wherever possible, data are checked as to the reliability of the test procedures used, and if such checks indicate the data are unreliable they will be discarded (i.e. inappropriate test conditions are assumed).

2. Properties of Substances taken into Account for Column B Ratings

Solubility, immediate reaction or predilution in water are factors which have always been taken into account for column B ratings. Compounds not killing test animals at their maximum concentration in (sea)water are rated as non-toxic. Compounds reacting immediately with water are assessed as their reaction products. Any predilution of substances with water is taken into account in calculating LC_{50} values for such solutions.

3. Ship Type Allocation (from IMO, 1986)

Ships subject to the Code should survive the normal effects of flooding following assumed hull damage caused by some external force. In addition, to safeguard the ship and the environment, the cargo tanks of certain types of ships should be protected from penetration in the case of minor damage to the ship resulting, for example, from contact with a jetty or tug, and given a measure of protection from damage in the case of collision or stranding, by locating them at specified minimum distance inboard from the ship's shell plating. Both the damage to be assumed and the proximity of the cargo tanks to the ship's shell should be dependent upon the degree of hazard presented by the products to be carried.

Ships subject to the Code should be designed to one of the following standards:

1. A type 1 ship is a chemical tanker intended to transport products with *very severe* environmental and safety hazards which require maximum preventive measures to preclude an escape of such cargo.

2. A type 2 ship is a chemical tanker intended to transport products with *appreciable severe* environmental and safety hazards which require significant preventive measures to preclude an escape of such cargo.

3. A type 3 ship is a chemical tanker intended to transport products with *sufficiently severe* environmental and safety hazards which require a moderate degree of containment to increase survival capability in a damaged condition.

Thus a type 1 ship is a chemical tanker intended for the transportation of products considered to present the greatest overall hazard and type 2 and type 3 for products of progressively lesser hazards. Accordingly, a type 1 ship should survive the most severe standard of damage and its cargo tanks should be located at the maximum prescribed distance inboard from the shell plating."

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APPENDIX 3

PRACTICAL EXAMPLES OF THE USE OF THE CHEMSPIL MODEL

The CHEMSPIL model provides a graphical representation or grid-plot (e.g. Figure A3-1) of the concentration-distance profile of the dissolved compound for different time periods i) at the moment that it has disappeared (see Figure A3-1) and ii) at the end of any subsequent time period(s) requested (Figure A3-2). This grid-plot represents half of the vertical cross-section of the circular plume of contaminated water where the top left corner (0.0) of the grid-plot represents the point of spill and thus the centre of the plume. Each grid-block of the plot represents an annular water compartment, the centre grid-block being a cylinder. The annular spacing is the same for each grid-block so their volumes increase going from the centre outwards. The grid-plot is displayed on the screen and plotted or printed if so specified. The shades give an indication of the concentration of the chemical. The different levels of shading represent: concentration (1) greater than the LC_{50} value, (2) between the LC_{50} value and 0.1 LC_{50}, (3) between 0.1 LC_{50} and 0.01 LC_{50} value, and (4) below the 0.01 LC_{50} value. This plot also provides information on:

- the name of the chemical,
- the volume of the spill,
- the maximum concentration,
- the time lapse since the spill occurred,
- the fraction in % of the spill that has dissolved,
- the fraction in % of the spill that has evaporated.

The following examples of calculations illustrate that for three compounds of similar aquatic toxicity but different physico-chemical properties, the outcome of a spill can be very different in concentration and in duration. Hexane was chosen to represent a poorly water soluble, low density compound with a relatively high vapour pressure, typical of the aliphatic hydrocarbon compounds which this report addresses. Aniline was chosen as a relatively water soluble, low vapour pressure compound with a density close to that of seawater. Benzene represents an aromatic hydrocarbon compound whose properties lie between those of aniline and hexane. For all three compounds, the LC_{50} was set at 5 mg/l, the wind speed at 10 m/s and the spilled volume to 60 m^3. For the seawater properties, spreading and dispersion behaviour, the default values of the program were accepted. In addition to melting point, boiling point and molecular weight, the following physical-chemical data were used:

compound	density kg/m^3	vapour pressure Pa	water solubility kg/m^3
aniline	1020	40	34
benzene	877	10,000	1.8
hexane	660	16,200	0.008

In Figures A3-1, A3-2 and A3-3 the spill situation for aniline, benzene and hexane, respectively, are shown at the maximum extension of the surface layer (slick) just at the moment this layer disappears. At that moment, the volumes contaminated vary significantly between the three compounds. Thus for aniline an area of some 200 m in radius is contaminated above $0.01 \times LC_{50}$ while for benzene the area is of 90 m radius and for hexane this level is not reached at all.

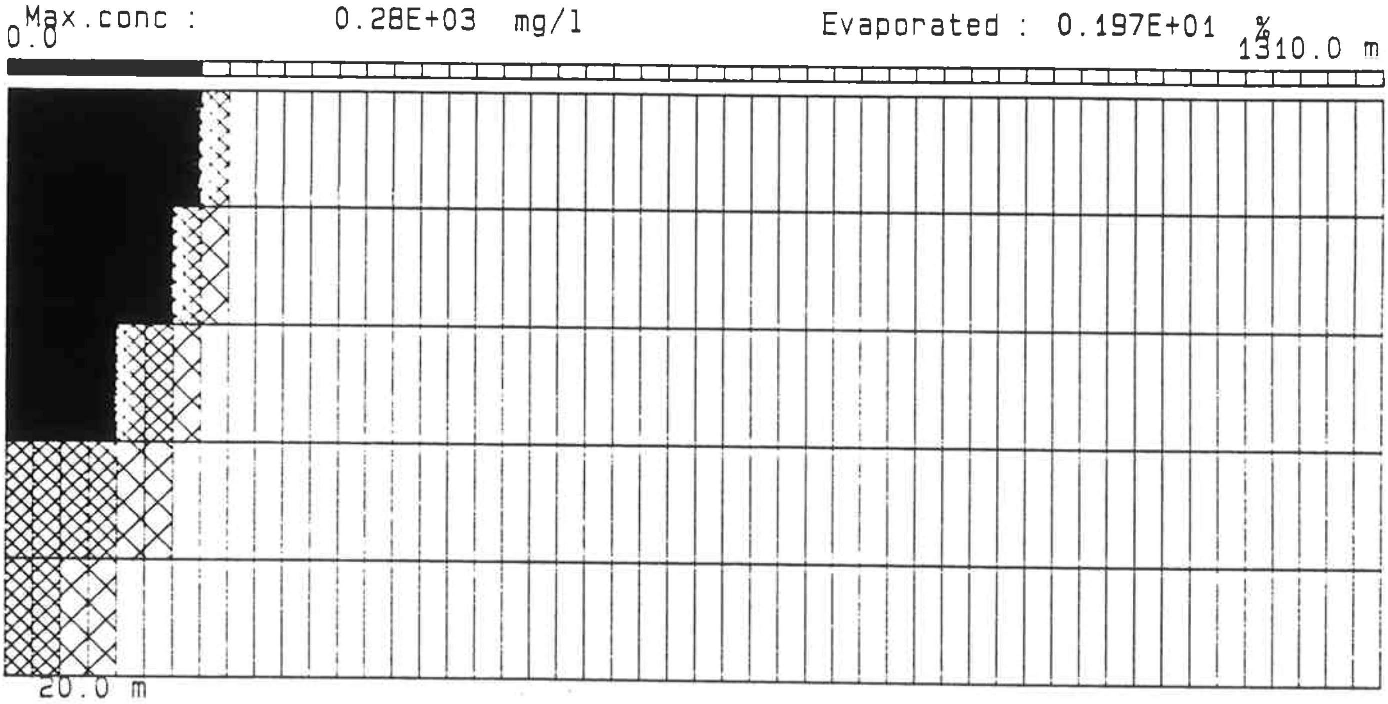
The benzene and hexane spills do not extend further after this time but for aniline the area contaminated continues to increase and its maximum extent is shown in Figure A3-2. These figures illustrate that for a spill of the same volume of product, the maximum volume of the sea contaminated and the time period that contaminant concentrations remain above certain levels can vary greatly for different products. For aniline, benzene and hexane, the maximum volumes contaminated at above the LC_{50} level are 3.9×10^6, 6.7×10^4 and 0 m^3, respectively.

The time course of the volume contaminated at above the LC_{50} level for aniline is illustrated in Figure A3-5. A further comparison has been made between aniline and benzene by calculating the volume of water contaminated above the LC_{50} by benzene at different spill volumes. This is illustrated in Figure

A3-6. From this figure it emerges that it would require a spill of 4400 m^3 of benzene to contaminate above the LC_{50} level the volume of sea (3.9×10^6 m^3) contaminated following a spill of 60 m^3 of aniline.

Figure A3-1

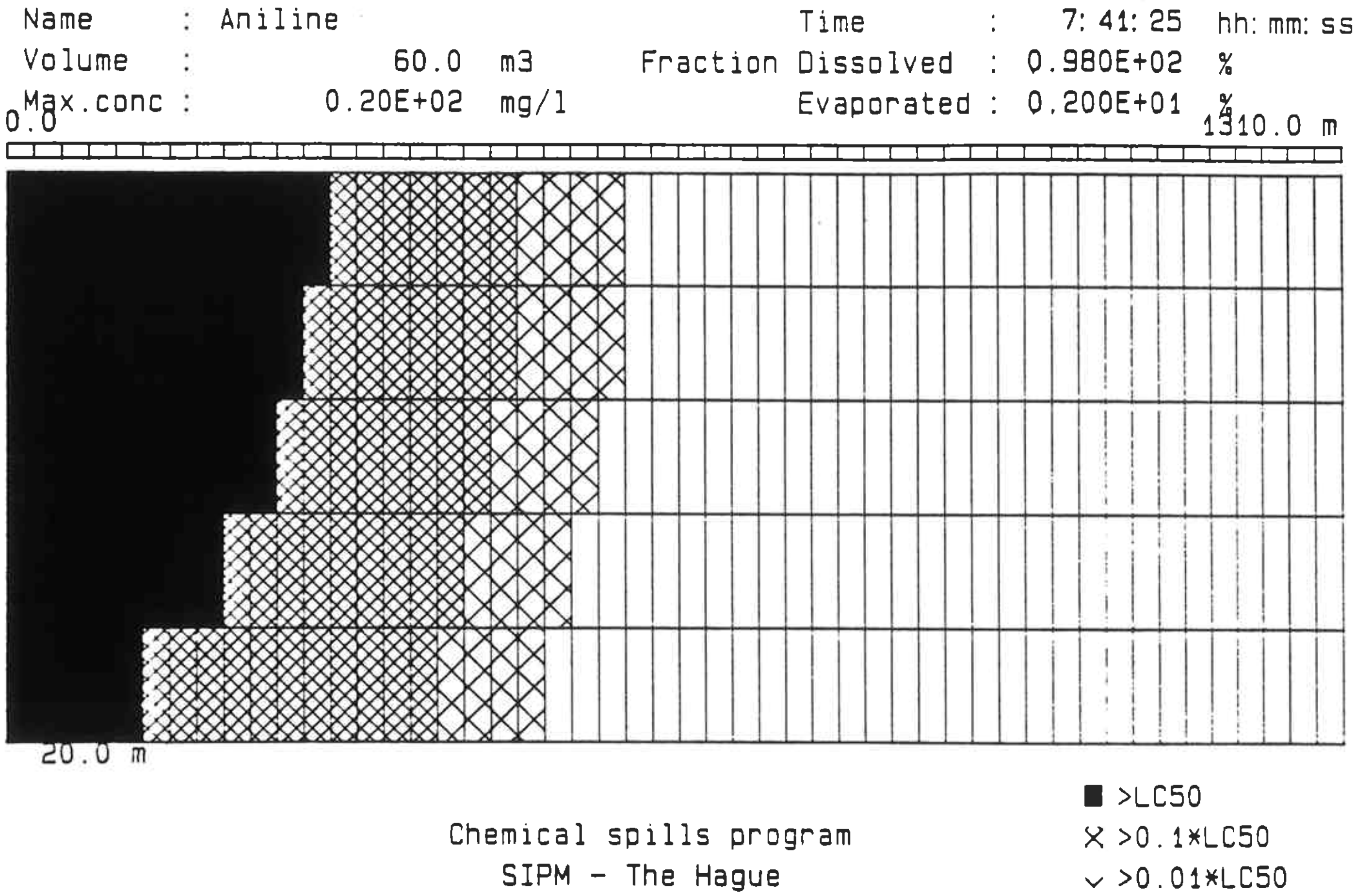
```
Name      :  Aniline                              Time           :    1: 41: 25  hh: mm: ss
Volume    :                60.0  m3       Fraction Dissolved     :  0.980E+02   %
Max.conc  :           0.28E+03  mg/l               Evaporated    :  0.197E+01   %
```



Chemical spills program

■ >LC50
✕ >0.1*LC50
✓ >0.01*LC50

Figure A3-2



```
Name       :  Aniline                              Time          :     7: 41: 25  hh: mm: ss
Volume     :                 60.0   m3      Fraction Dissolved   :  0.980E+02   %
Max.conc   :          0.20E+02   mg/l              Evaporated    :  0.200E+01   %
```

Chemical spills program
SIPM - The Hague

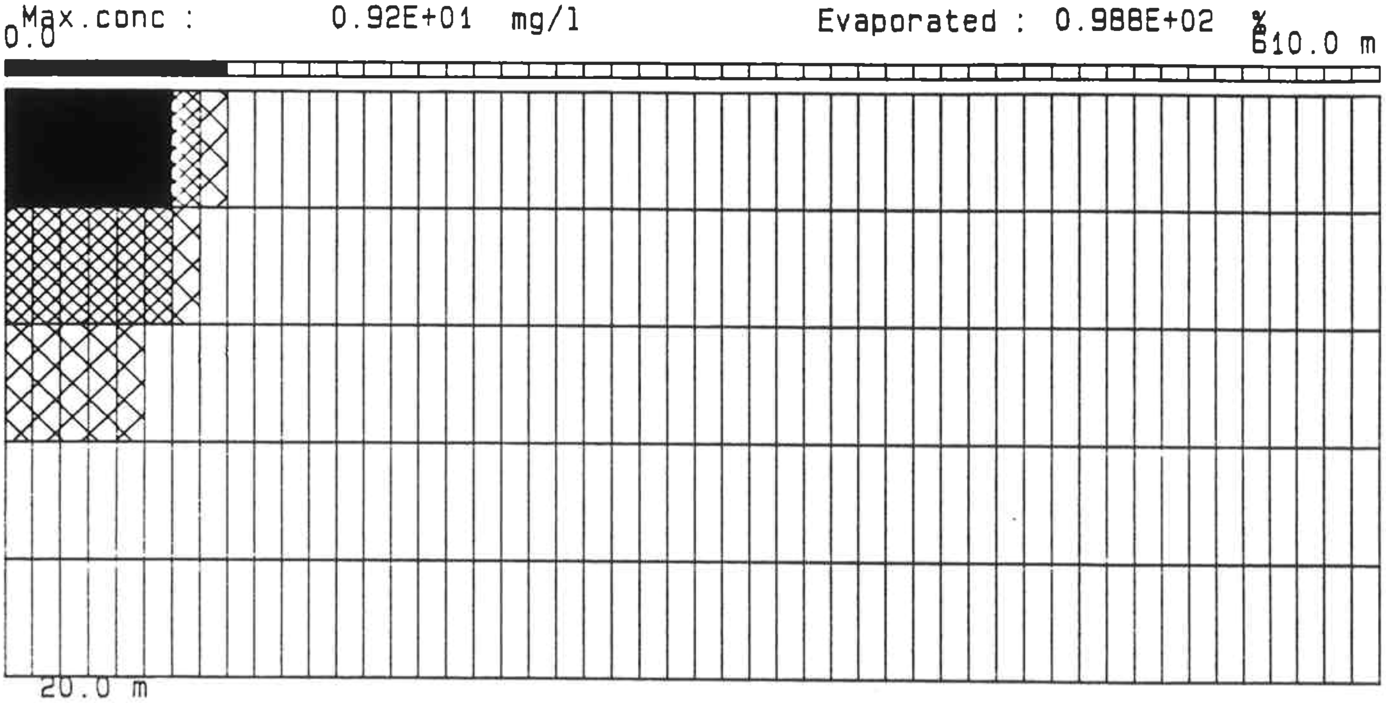


Figure A3-3

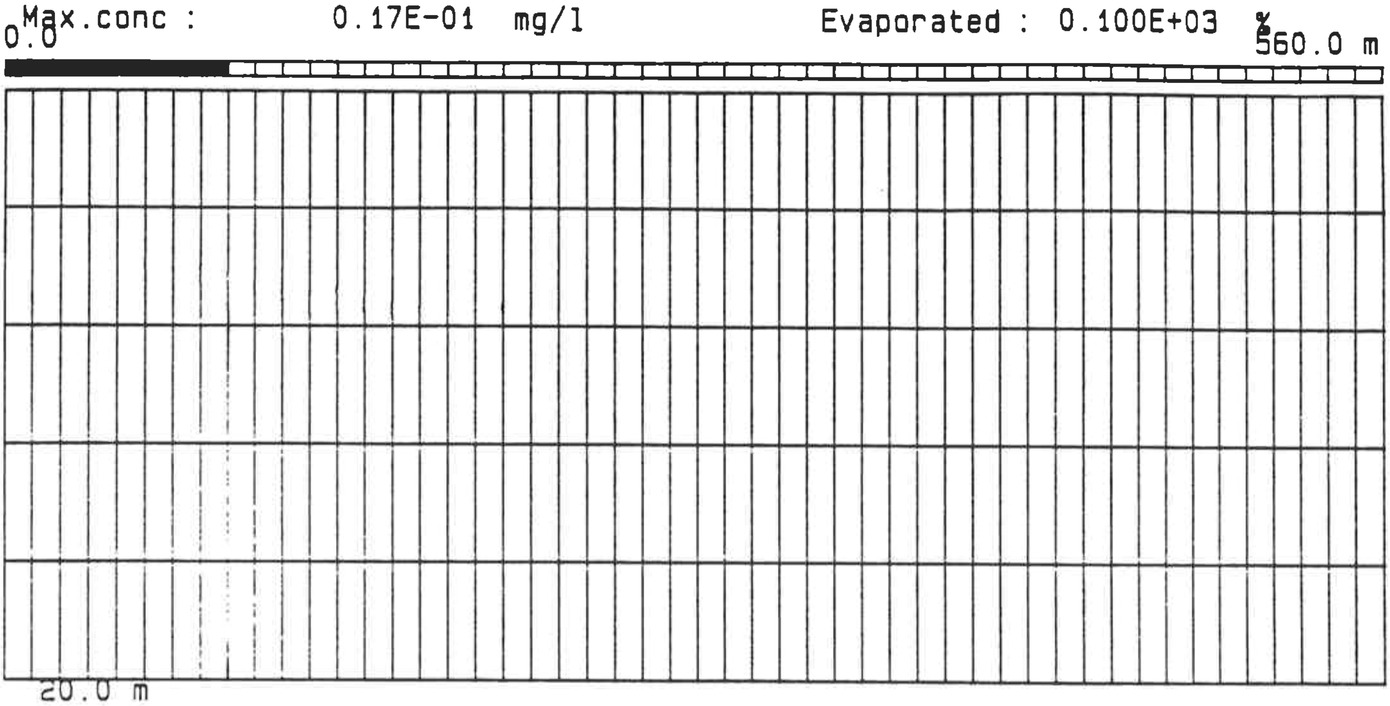
```
Name       :  Benzene                                  Time            :     0: 33:  4  hh: mm: ss
Volume     :                 60.0  m3      Fraction Dissolved  :  0.120E+01  %
Max.conc   :           0.92E+01  mg/l               Evaporated :  0.988E+02  %
```

■ >LC50
✕ >0.1*LC50
✓ >0.01*LC50

Chemical spills program
SIPM - The Hague

Figure A3-4

```
Name      : Hexane                                 Time           :    0: 15:  7  hh: mm: ss
Volume    :                 60.0  m3      Fraction Dissolved      : 0.240E-02  %
Max.conc  :            0.17E-01  mg/l              Evaporated     : 0.100E+03  %
```



■ >LC50
✕ >0.1*LC50
✓ >0.01*LC50

Chemical spills program
SIPM - The Hague

Figure A3-5

VOLUME OF WATER CONTAMINATED ABOVE LC50 AFTER ANILINE SPILL OF 60 m3

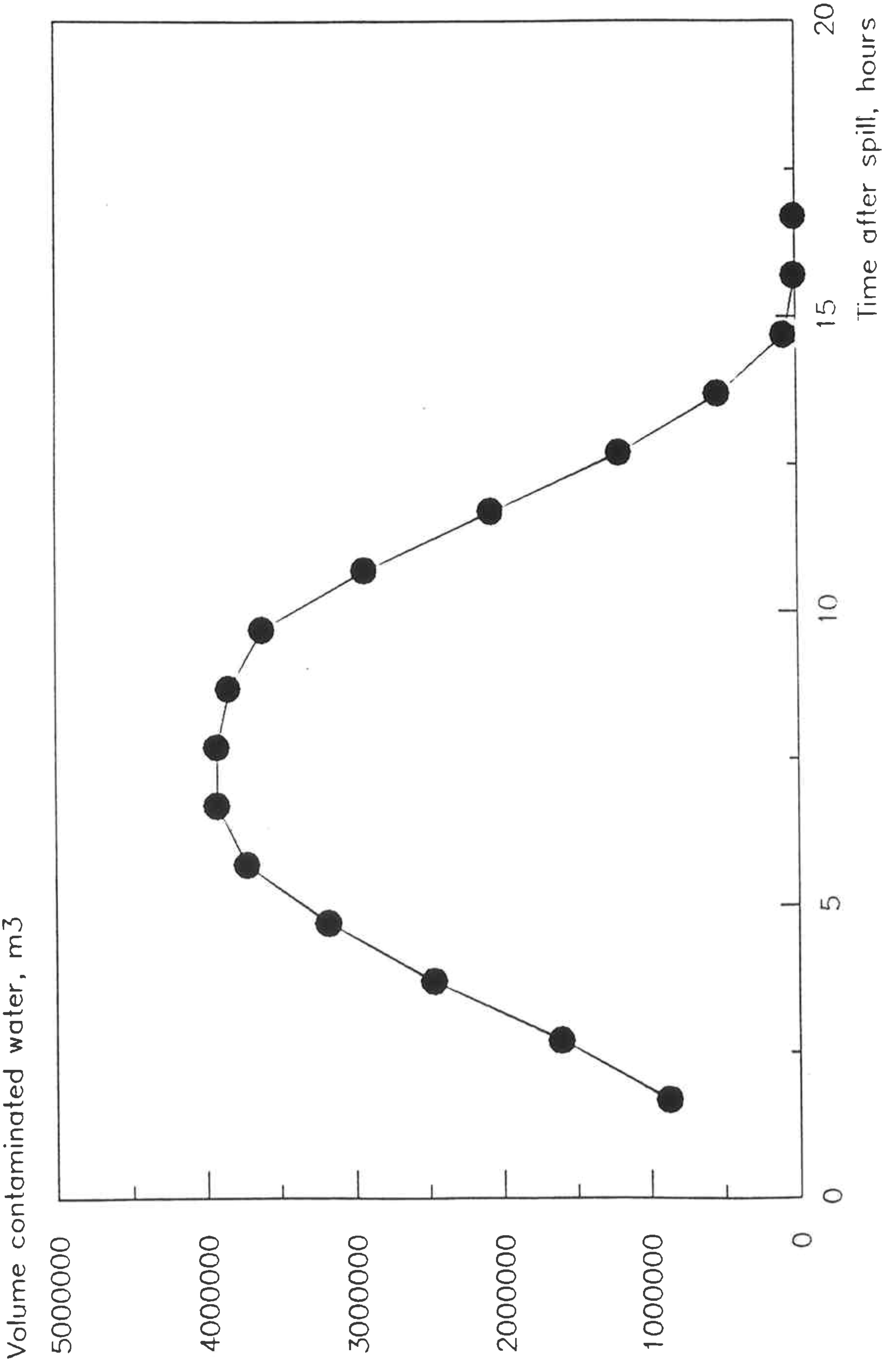
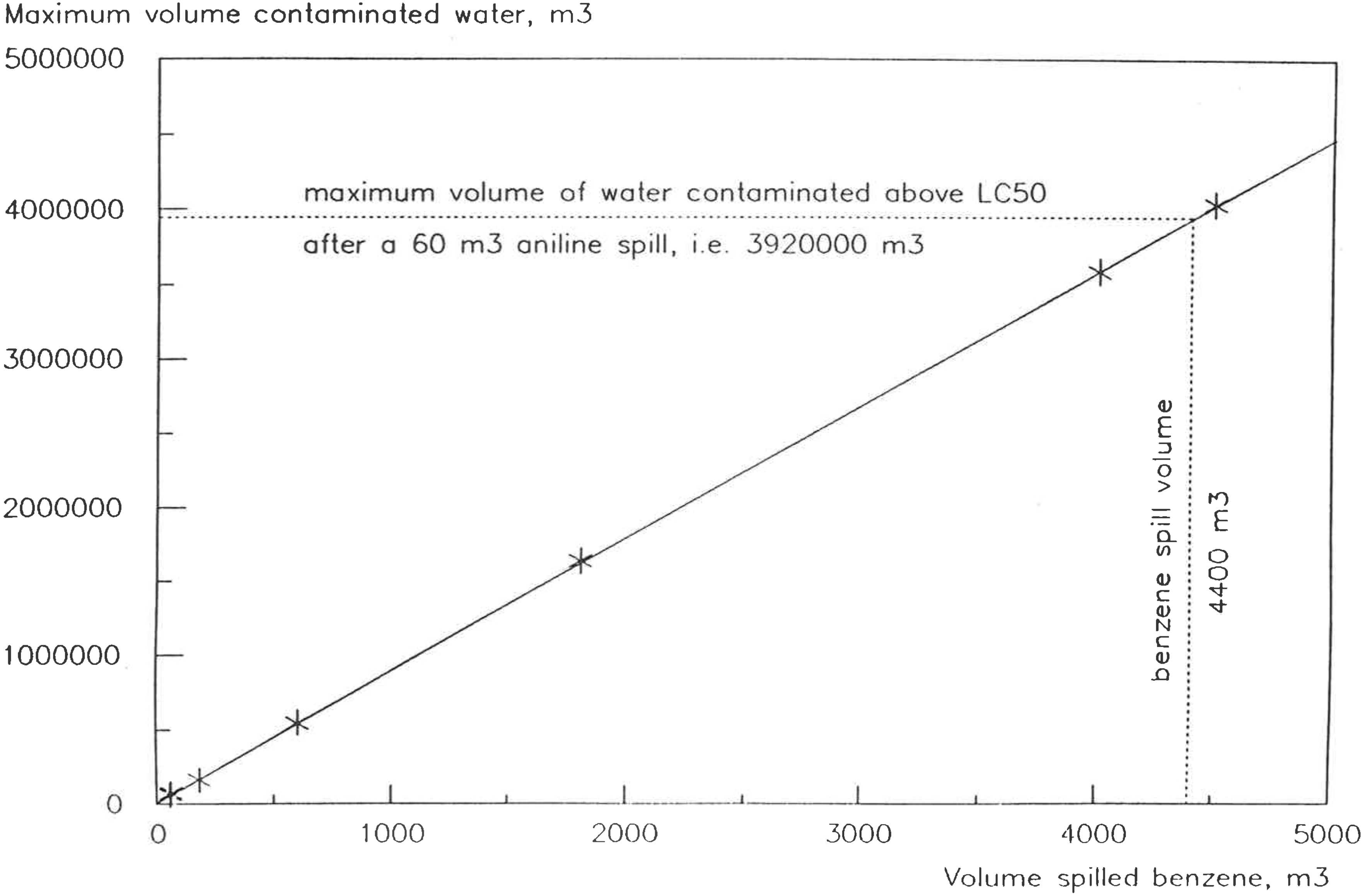


Figure A3-6

MAXIMUM VOLUME OF WATER CONTAMINATED ABOVE LC 50 AFTER BENZENE SPILL; DIFFERENT VOLUMES



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D-1990-3001-67

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