



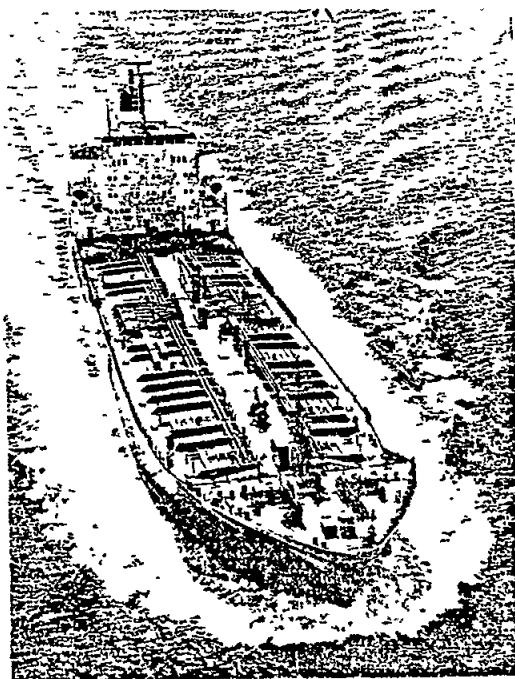
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**RISK ASSESSMENT OF MARINE CASUALTIES**  
**INVOLVING HAZARDOUS SUBSTANCES**  
**IN THE MEDITERRANEAN SEA**  
**- AN OVERVIEW-**

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**RISK ASSESSMENT OF  
MARINE CASUALTIES INVOLVING HAZARDOUS  
SUBSTANCES IN THE MEDITERRANEAN SEA**

**ABSTRACT**

The risk assessment of an accident involving ships transporting chemicals in the Mediterranean is related to the amount of traffic of specialized carriers in certain areas ; the main routes are the longitudinal routes Suez-Gibraltar and Bosphorus-Gibraltar which have the most concentrated circulation and the transversal routes connecting the main petrochemical complexes in the southern Mediterranean to Marseilles-Fos, Genoa and Trieste which are connected with the South European pipeline. A significant coastal navigation is also associated with these major routes and chemicals are heavily transported along the French, Spanish and Italian coastlines.

Liquefied gas is the major product which is transported in terms of weight and its traffic is especially large in the Adriatic sea and around the Italian peninsula.

Among the organic chemicals most transported, in terms of their tonnage, we note methanol, ethanol, benzene, ethylene-glycol, styrene, xylene and toluene. The inorganic chemicals are mainly sodium hydroxide, phosphoric acid and sulfur.

The packaged chemicals (data taken from the Marseilles-Fos port complex) only represent 2.5 % of the total tonnage (the remaining 97.5 % is covered by bulk-including LG-transport) ; however, more than 40 % of the movements (calculated on the frequency per chemical) are involved with packaged chemical transportation. Thus, the same ship could carry a large variety of chemicals which have been packaged, although not in large quantity ; the most often carried are anhydrous aluminium chloride, arsenious anhydride, barium chloride and sodium cyanide.

A classification of these products in three categories (liquefied gases and volatiles listed in the IGC code, other products which can be transported in bulk and packaged chemicals) was done on the basis of their transported weight, as well as on the basis of the frequency of their movements and on the basis of those products which are the most hazardous for man and his environment.

The likelihood of a spill, for each product and for each group of chemicals was calculated on the basis of casualties which have previously occurred, for all the ships of more than 100 GRT, in the Mediterranean, between 1978 and 1982. In this way, the likelihood of an accident has been determined to be 0.03 % per year for the entire Mediterranean, which is about 10 per year for the ships carrying chemicals and liquefied gases.

The accident case studies of chemical spills have shown that these accidents are, in fact, even less than was expected from the risk assessment figures. However, recent examples of accidents show that the losses of chemical containers which have been loaded onto the deck are increasing.

• If we believe that the Mediterranean, on the basis of its hydrological and ecological characteristics, is a vulnerable sea, especially when compared with an oceanic zone - and especially near the coastline where the greatest amount of traffic is concentrated, measures must be taken to predict and prevent major risks in the case of an accident.

It is notably in this light that the members of the task force n° 8 in the COST-301 program are trying to precisely evaluate the amount and the nature of maritime transportation in the Mediterranean. (In this report we also present an overview of the problems associated with combating marine pollution by hazardous substances.) Also, in order to improve cooperation among the Mediterranean neighboring countries, both in the prevention of accidents as well as in controlling and cleaning-up any eventual hazardous spills, ROCC needs to play a determining role as it does in the area of oil spills.



**RISK ASSESSMENT OF  
MARINE CASUALTIES INVOLVING HAZARDOUS  
SUBSTANCES IN THE MEDITERRANEAN SEA**

**1. INTRODUCTION**

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At the request of the International Maritime Organization (I.M.O), an overview paper, concerning the risk assessment of marine casualty involving hazardous substances other than oil, carried by ships in the Mediterranean, has been done by the French Centre de Documentation, Research and Experimentation on Accidental water Pollution (Centre de Documentation, de Recherche et d'Expérimentation sur les Pollutions Accidentelles des Eaux-CEDRE)The contract was signed on december 17, 1986 and the study involved approximately 2 engineer - months of work.

Such a preoccupation is due to the increased use of man-made chemical products in industry or agriculture and the obvious consequence of increasing their transportation. The risks related to the maritime transportation of the substance are two fold with the increased tonnage as well as an increased number of movements. An increased risk of casualties, an increase of dangers for both the crew and the rescuers, and, finally, an increase of menaces to marine resources are the resulting corollaries.

Although all these risks have been fairly precisely evaluated for certain areas of the world's ocean, on the contrary, in the Mediterranean, very little information is available at this time.

The purpose of this study is :

- to present an overview of the situation of maritime transportation of chemical products in the Mediterranean, both in bulk and packaged.
- to evaluate the likelihood of an accident for ships transporting chemical products and liquefied gases, and to define the factors specific to the Mediterranean area.

- to know which hazardous substances have the greatest possibility of being spilled and in what quantity.
- to summarize what threats are posed to man and his environment by an accidental chemical spill.
- to inventory the information available on the techniques used for a hazardous chemical spill control.

The conclusions of this study provide indubitable arguments for the :

- prevention of accidents (an increased surveillance with appropriate methods in high risk zones) ;
- optimization of intervention in the event of a hazardous spill (ensuring the safety of human lives both for victims as well as rescuers as well as prompt action to mitigate damage to the environment) ;
- use of operational procedures with a maximum effectiveness and speed.

This orientation should also furnish information

- which will improve existing contingency plans
- which will assure a training program for anti-pollution personnel.

## 2. GENERALITIES

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### 2.1 Definition of a "marine casualty".

It is common practice to distinguish between the marine casualties which are "serious" from those which are not. It is, in fact, on the basis of this separation that Lloyd's Shipping Information Service prepared a classification and published it in the "Tanker Casualty Bulletin".

Certain basic definitions are listed below :

- MARINE CASUALTY                    Any incident to a propelled, sea-going merchant ship of 100 tons gross and above in which the condition of the ship suffers adversely.
- MARINE TRAFFIC (RELATED) CASUALTY    The initial casualty types ; collision, contact/ramming, wrecked/stranded.
- SERIOUS CASUALTY                    A marine casualty which results in :
  - a) Structural damage, rendering the ship unseaworthy, such as penetration of hull underwater, immobilisation of main engines, extensive damage, etc.
  - b) Breakdown necessitating towage or shore assistance
  - c) Actual total loss of vessel
  - d) Any other undefined situation resulting in damage or financial loss which is considered to be serious.

Several possibilities exist for studying the risk assessment of Marine Casualties. One assessment study, done by the "BUREAU VERITAS" in 1985 at the demand of CEDRE and IFREMER, characterized the probability of pollution, associated with all potentially dangerous ships in a well defined maritime area (several hundred kilometers). The methods used by the BUREAU VERITAS, described in Annex I, deal successively with :

- a definition of pollution processes
- an estimation of accident rates which are characteristic for various types of transport ships
- a calculation of the probabilities of pollution.

Studies of reliability or of security, based on the methods of the "failure tree" and on the "failure mode and effect analysis" (F.M.E.A.) rely on a precise and complete knowledge of data such as : the tonnage and the nature of the products which are loaded or unloaded in port, the frequency of their transportation, their packaging, the characteristics of the ships used for transport (size, structure, means of navigation, age, upkeep, commissioning, flag state, etc), the routes which are used, the amount of traffic, the means of surveillance, the means of rescue and the meteo-oceanological conditions.

The methodology used by the Canadian Coast Guard in its study "Vessel Traffic Service" has given a definition of a risk index and the probabilities of an accident. According to this study, the probability of an accident endangering a ship (i) in a given area (j) is the result of the "danger factor" of the area (aj) multiplied by the average accident rate for the ship in category i. All these terms have been carefully defined in a statistical manner on the basis of available information regarding the transported products, the ships or the environmental parameters.

Such risk assessment studies have their origin in investigations adapted by the port authorities or other organizations dealing with a centralization of detailed information. Available information in data banks have up to now been sparse or incomplete, especially in regard to transportation of chemical substances.

According to a CEDRE Report (1982), the methods normally used in risk assessment have been shown to be inoperable. It proposes that the study begin by an inventory of all the accidents and incidents which have already taken place and which are able to cause coastal pollution. The predominant idea is that any catastrophic accident is preceded by accidents or incidents which are warning signs. In paying attention to the warning events, it should be possible to prepare meaningful scenarios and thereby predict the catastrophic events.

The Maritime Research Institute of Hamburg (Forschungsstelle für die Seeschifffahrt zu Hamburg-FSSH) elaborates "model accidents" based on accidents which have or have not caused real pollution.

Two flow charts summarizing a preliminary risk assessment and an accident scenario are presented in Annex II. They present possibilities of major sea casualties along with their causes and consequences.

The event tree which was obtained for sea casualties (CEDRE Report, 1982) has up to 19 levels of decomposition, 254 root events and 173 intermediate events. This method is also applicable to marine casualties involving chemicals on the condition that the totality of "root events" is really known. A list of fundamental events is given in Annex III.

## 2.2. Method used for risk assessment

The methodological approach used in this study is more general ; it is near that presented by the Dutch RIJKSWATERSTAAT (1984, 1986) which distinguishes the "relative risk", based on the maritime traffic (tonnage and frequency) from the "absolute risk" based on the frequency of accidents. In the present report, we do an analogical comparison of the number of accidents which affected all ships.

This method is easier to use when the nature of the transported chemicals and their tonnage are defined and quantified for one port. In the case of the Mediterranean, it is necessary to know precisely the flow of transportation for chemicals from port to port, or the transit traffic across the Mediterranean.

Such an inventory has not yet been done. A start has been made in this area within the framework of the "COST 301" program and information is centralized at the calculation center of the Navigation Institute of Automation (Istituto per l'Automazione della Navigazione) in Genoa, under the responsibility of Professor E. Volta.

As of January 1987, the data collected in Genoa are limited and also inaccessible because the Institute is in the process of acquiring a new computer in order to evaluate the data and then to prepare a recapitulation of the maritime routes used by the tankers carrying chemical substances.

The only precise information which we have come from the area Marseilles-Fos : approximately 150 Liquefied gases and other chemicals transported in bulk, and in a packaged form (of more than 10 tons per load) have been inventoried.

The port of Marseilles-Fos, largest Mediterranean port, 2nd largest European port and 6th largest in the world, drains a large part of the maritime transportation of hazardous chemicals. Due to the diversity of the products which are handled and to the diversity of the industry which is located in the surrounding area (Lavéra, Port de Bouc), the chemicals identified in this zone give an idea of the sorts of products which circulate in the Mediterranean. (Specific information which has been obtained in the literature and which relates to substances transported through the Suez Canal or shipped from African coasts will also be taken into consideration).

Concerning traffic density, we will use existing data on maritime traffic of merchandise in general or for petroleum. Although the oil tanker circulation does not always correspond to that of chemical carriers, an observation of their maritime routes, the amount of traffic, and the localities of the principal petro-chemical complexes on the Mediterranean coast will also give an idea of hazardous chemical transportation routes.

A classification of the chemicals has been made according to

- The frequency of their transport which enables a risk assessment for their being spilled
- The tonnage and the chemical properties which enable a risk assessment for man and the environment in the event of spillage
- The age of the ships transporting the chemicals enable an identification of the chemicals carried by high risk carriers. Three distinct lists have been drawn up : one for liquefied gases, one for bulk transport and one for products which are packaged.

Finally, an estimation of accident frequency specific to the Mediterranean sea will enable a calculation for a risk of release of a given chemical during a given period.

The consequences of a marine casualty -which should be taken into consideration in all risk assessment studies in the same way as the possibility of accident- will be covered later.

### 2.3. Definition of the expression "hazardous substances" (other than hydrocarbons)

The term "hazardous substances", as well as their transportation in bulk or in packages, has been defined in numerous international conventions. We distinguish here, among the chemical products :

- liquefied gases : LNG and LPG, as well as volatile liquids (Bp<35°C) listed in the IGC Code.
  - bulk chemicals, whether they are liquid or solid
  - chemicals carried in a packaged form.
- (Radioactive products are not covered in this study)

"Substances other than oil" have been defined in the "protocol relating to intervention on the high seas in cases of marine pollution by substances other than oil, 1973" of I.M.O.

Annex IV, which is taken from the report of the Maritime Institute of Hamburg, entitled "Relation Between the Conditions of the Maritime Transport of Dangerous Goods and the Protection of the Marine Environment", contains definitions and information regarding hazardous substances.

### 3. BIOGEOGRAPHIC FRAMEWORK AND METEO-OCEANOLOGICAL CONDITIONS OF THE MEDITERRANEAN SEA

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As is well-known, the Mediterranean sea has a quasi-closed basin, with just one natural doorway (Gibraltar) on the Atlantic Ocean and a smaller, artificial doorway (Suez Canal) on the Indian Ocean. It also features a few "check points", like the gateway between West and East areas (Sicily Channel and Messina Straits), and the gateway (Bosporus) to the Black Sea.

It is 3.800 km long, and 800 km wide when measured between the Gulf of Genoa and Tunisia. The volume of water is 4.24 million km<sup>3</sup> and its area is 2.996.000 km<sup>2</sup> (including the Black Sea), which represents 1/180 part of the total surface of the world's oceans and seas (map n°1). The most dominant characteristic is the steep descent of the coast lines towards the oceanic plains at the center of the major basins with a depth varying from 2000 to 3000 m. However, the average depth of the Mediterranean is approximately 1500 m. The Mediterranean is divided into two large basins, west and east, which are separated by the sicilian-tunisian shelf.

The width of the strait of Gibraltar is 14.5 km and its depth is approximately 160 m. This strangling bottle neck makes a water exchange with the Atlantic Ocean difficult (the Mediterranean waters are renewed every 80 to 100 years). Despite its size, the Mediterranean, due to the narrow opening, is characterized as a half-closed sea whose waters are enclosed in an area composed for 99 % by a continental land mass. It is, therefore, a sea which is almost independant. Situated in a subtropical climate with a large amount of evaporation, and







Map nr. 2 - Main currents in the Mediterranean Sea  
 (source ROCC-Mediterranean action plan)

having a rain and river contribution which is too small (about 2200 km<sup>3</sup>) to compensate for evaporation (approximately 5200 km<sup>3</sup>), the water level would be diminished by almost 1 m per year if the sea was not in communication with the Atlantic Ocean via the Strait of Gibraltar. However, since the contribution of the ocean cannot completely compensate for the loss by evaporation, the water is saltier (about 1 g. more per liter) and the salinity increases with distance from Gibraltar (with local variations at the mouths of the major rivers).

Along its 20,000 miles long seaborder, three Continents (Europe, Africa and Asia) face each other, flying twenty different national flags from their 284 ports of varying size. Twenty countries, sometimes divided by various political, economical and technological situations are united by their common interest to maintain the freedom of navigation in a safe sea which is a guarantee for their economic support.

Fundamental reasons make the Mediterranean case very distinct from the North-European one, as pointed out by WG8 of COST-301, i.e. : the climatic, tidal, and biological conditions, the sometimes peculiar traffic flows, the heterogeneous technological level of ports and service centres, the various sensibilities of governments involved, etc.

Contrary to the Atlantic coastline where the currents are related to the tides, in the Mediterranean the wind is almost always responsible for the direction and speed of the sea's currents. The Mediterranean currents rarely exceed a speed of 1 knot. The surface currents have a cyclonic circulation with currents from the West to East along the African coast and from East to West along the European coast (Tchernia, 1980). This general circulation pattern can be completed by coastal counter-currents which are quite variable and depend on meteorological conditions (map n°2).

In the north-east area of the western basin, including the Ligurian sea, the Gulf of Genoa and the Tyrrhenian sea, there is a regular current called the "Ligurian current" which occurs independently from wind conditions. With an average speed of less than 30 cm/sec, it flows from east to west along the French coast line from Monaco to Lion gulf. A large whirlpool is located between the continent and Corsica, and this causes the current to flow in a north-east direction on the north-west coast of Corsica. In the strait of Bonifacio a tidal current with a force of 2-3 knots has been observed, but this is an exceptional and very localized phenomenon.

Despite the small size of the tides (20-30 cm), an increase in the sea level could be significant during a bad storm ; this has been observed in the north of the Adriatic sea where the water level has occasionally increased by 2 meters.

According to information given in the "PLAN BLEU", in 1980, 862,000 tons of fish were declared to be caught from the Mediterranean (and this does not include the non-declared quantities which were consumed by the fishermen or sold locally). This quantity is equal to 1 % of the total world's fish catch.

Biologically, the plankton production is slowed by the lack of phosphates, nitrates and nitrites. Only a few large rivers which might carry these necessary nutrients flow into the Mediterranean (i.e. Ebro, Rhone, Po and Nile, the flow of which is greatly reduced by the Assouan dam and the irrigation canals). The sea water is relatively stable with a very slight mixing. Benthic and abyssal life forms are unplentiful : from 120 or 130 m deep, the Mediterranean is more or less sterile. Coastal pollution has contributed to a lowered fish population : the pollution or destruction of the posidonia has diminished the spawning of numerous species.

The Mediterranean is, however, a sea which is rich in species (450-500 as opposed to 170 observed in the Baltic sea). Approximately 120 species are caught by fishermen and some of them are probably over-exploited.

The clupeides (anchovies, sardines, etc) are more than half of the total catch, followed by mackerel. Shellfish are a little more than 15 % (by weight) of the total.

Also, the Mediterranean has an important potential for fish farming.

The diversity of species and the geographic isolation of the sea are two reasons for its ecological fragility. The vulnerability of the Mediterranean is due to its moderate size and accentuated by the ratio of its long coastlines to its water mass. In fact, Coastline pollution is the greatest cause for the Mediterranean pollution problem.

#### 4. THE MEDITERRANEAN MARITIME TRAFFIC

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##### 4.1 General considerations

The Mediterranean Sea was defined as a "special area" by an IMO Convention with regard to antipollution measures and in the light of possible ecological calamities as a consequence of shipping casualties.

Work conducted within the TRAMED 77 PROGRAM and group 8 of COST 301 \* (cf. ANNEX V) has enabled the traffic in the Mediterranean Sea to be considered as independant from traffic generated in other European seas, based on specific characteristics :

- pollution hazards are extremely critical due to the long renewal cycle of the waters, and due to the major economic role played by the tourist industry ;

\* The European COST 301 program dealing with the Mediterranean has covered the particulatities of this sea in terms of traffic circulation. We have used long passages of the COST 301 Reports in this study, especially those written by the Professor Volta's team in Genoa.

- traffic is of a 'captive' nature in the sense that inward as well as outward movements can easily be controlled in the basin ;
- vessels' navigation time between origin and destination in the Mediterranean is generally not more than two days ;

Apart from geographical characteristics, Mediterranean traffic also has some specific aspects which can be summarized as follows :

- The coexistence of various kinds of traffic, such as large ships (tankers etc.), crossing commercial traffic (such as ferries etc.) and small leisure and fishing boats in the same area.
- The very scarce use of traffic separation schemes.
- The absence of harbours with long approach channels.
- The presence of traffic which is just transiting across the sea and not landing in any port.

Approximately 600 vessels circulate every day in the Mediterranean, i.e. 1/3 of the world's oil-tanker traffic and 1/6 of the international maritime commerce (Journal de la Marine Marchande, January 9, 1986).

For the North Atlantic, the traffic of petroleum products, liquefied gases, and bulk chemicals is \* :

- . 60% of the ships carry petroleum products (90 % of the tonnage)
- . 20% of the ships carry liquefied gases (6.5 % of the tonnage)
- . 20% of the ships carry bulk chemicals (4.5 % of the tonnage), especially coasters of around 2,000 tons of capacity.

However, commercial exchanges of chemicals are very variable according to trade and dollar value fluctuations ; also the "special drawing rights" to be paid at the Suez Canal may lead a transporter to choose the route around Africa rather than a crossing of the Mediterranean sea. In addition, financial

\* The statistics have been done by CEPPOL on the basis of vessels traveling off the coast of Brittany.

interests related to the facilities of the Port of Rotterdam, free trade, could cause ships moving, for example, from Suez to Fos, to travel by way of Rotterdam.

#### 4.2. The principal maritime routes

Data analysis of transportation in the Mediterranean has been made by the Maritime Research Institute Netherlands (M.A.R.I.N.) in collaboration with the Danish Maritime Institute (DMI). Map n° 3 shows the principal maritime routes and the traffic flow in the Mediterranean. The major traffic route crosses the entire sea and passes close to the Algerian Coast. Another important route connects Suez with the northern Adriatic sea. If we observe all the maritime routes (map n° 4), only a few zones in the Mediterranean are unused by the carriers. Certain areas are significantly more dense, i.e. the zone surrounding the Italian peninsula. In addition to the routes shown on map 3, those connecting the major Italian ports with petrochemical industrial complexes, particularly Skida, Marsa-El-Brega and Marseille-Fos, are shown on map n° 5.

Data collection from several sources enabled the elaboration of map n° 4, where the principal trade routes in the Mediterranean have been centralized.

Although the East-West routes (such as Suez-Gibraltar, Dardanelles-Gibraltar or Suez-Adriatic) are very much traveled, the north-south crossings are also heavily used. These trade routes are especially related to petroleum products transportation. Concerning North South routes, the most heavily traveled connects Skida, in Africa, to the Ports of Tarragone, Marseilles-Fos, Genoa and Trieste ; these last three areas are relay zones for the south-European pipeline. Other north-south routes going from Marsa-El-Brega and Marsa-El-Hariza are less densely traveled. (map n° 4).

In addition to these trans-mediterranean routes, we note a large Coastal circulation.

The report prepared by the M.A.R.I.N. gives a precise idea of the traffic patterns in the Mediterranean including zones such as the Bosphorus, the Strait of Messina and the Strait of Gibraltar. A large amount of data concerning the "Sub-areas" are also available in the COST 301 program reports.

On map n° 6 the routes used around Corsica, including the Strait of Bonifacio - between Corsica and Sardinia - have been traced.

This traffic evolves from one year to the next and also from one season to another. The table below, taken from an Italian report of the COST 301 (VII/417/85), shows variations in ship movements recorded for summer and winter in Italian territorial waters :

ship movements

<u>type of ship</u>	<u>January</u>	<u>July</u>
Ferries	883	2171
Gas carriers	253	179

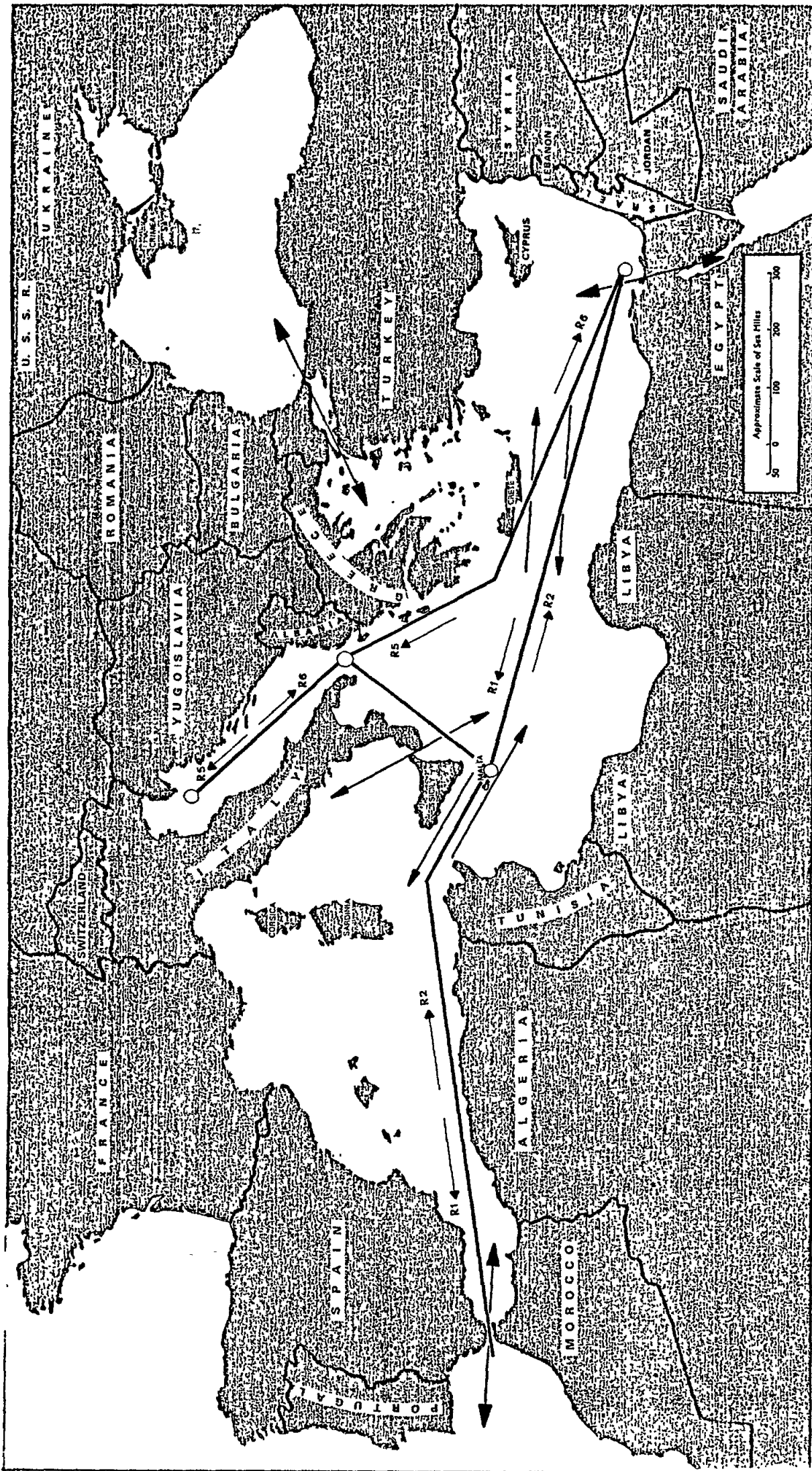
The maritime transportation of liquefied gases is greater in winter when the need for heating is greater, while the Ferry-Boat circulation is greater in the summer with the increase in tourism.

#### 4.3 Maritime traffic of liquefied gases

The maritime transportation of liquefied gases is relatively well known. On map n° 7, the main routes used by LNG-LPG carriers as well as the principal coastal cities having a pipeline for natural gas are shown.

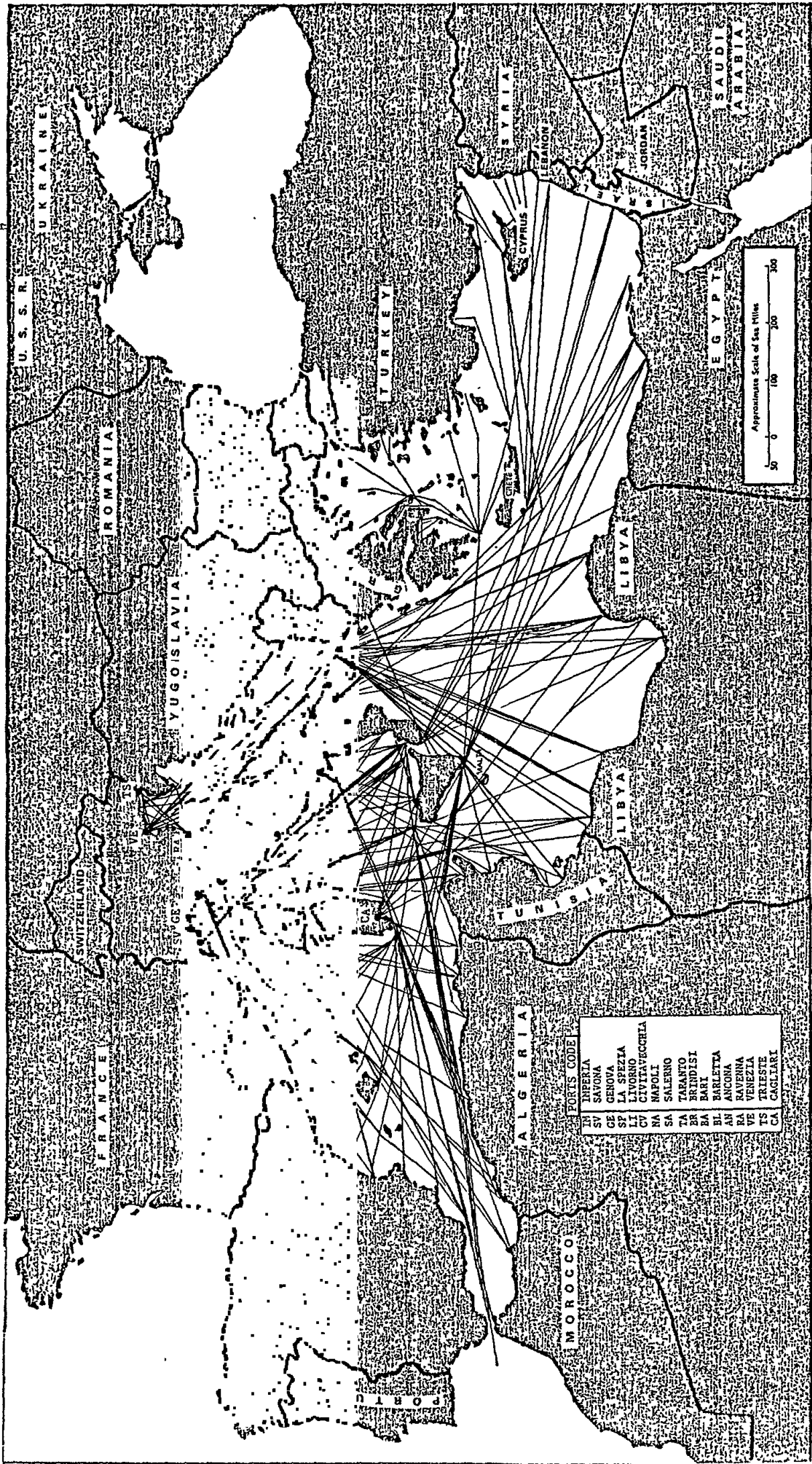
The supply of natural gas or petroleum for south-Europe comes from the gas fields and refineries located in Venezuela (via Gibraltar), from Saudi-Arabia (via Suez), from Algeria (Skida) or Tunisia (Cap Bon). The principal trade routes used by the methane



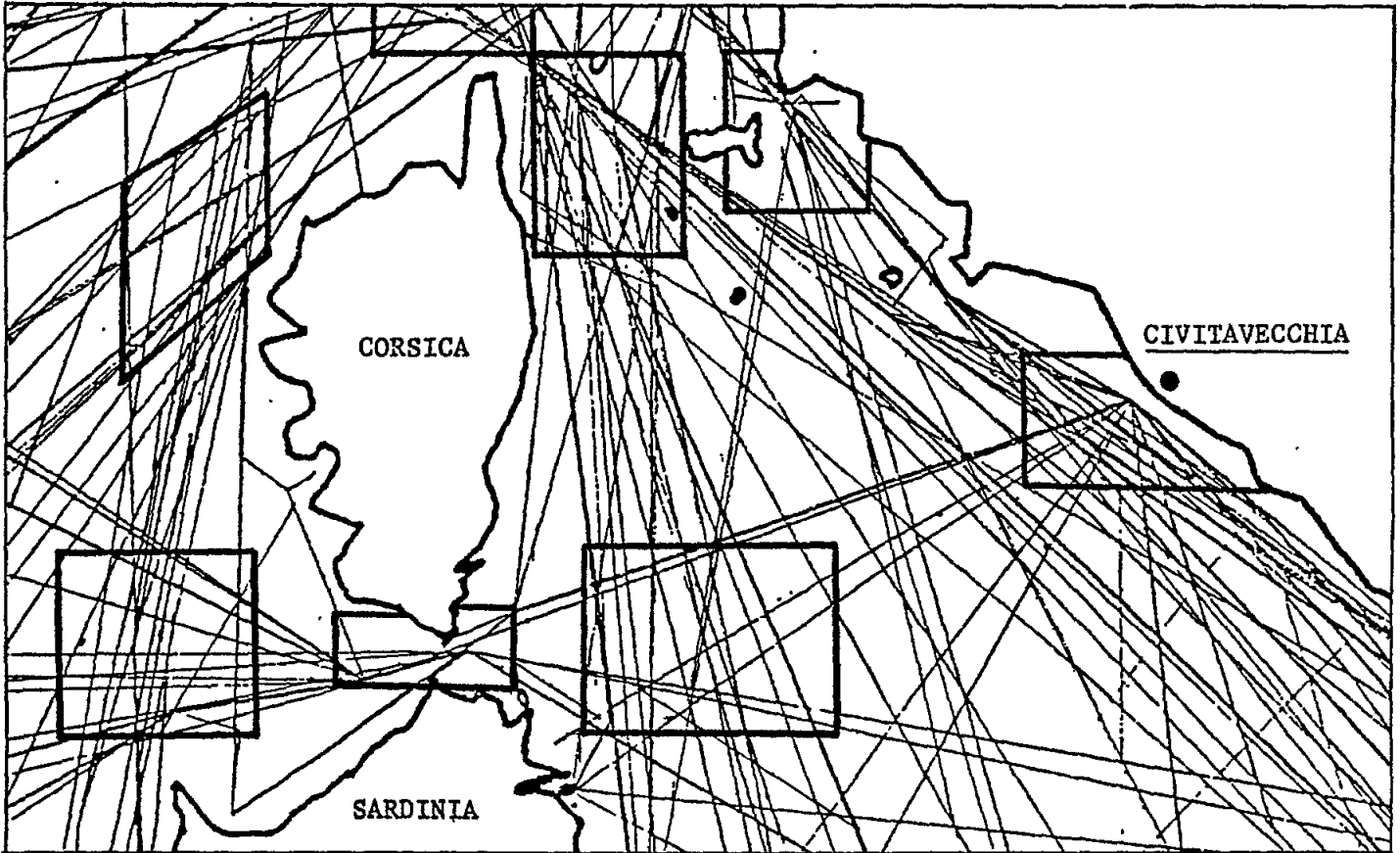


Map nr. 3 - Main routes and traffic flows in the Mediterranean Sea  
 (source COST 301)





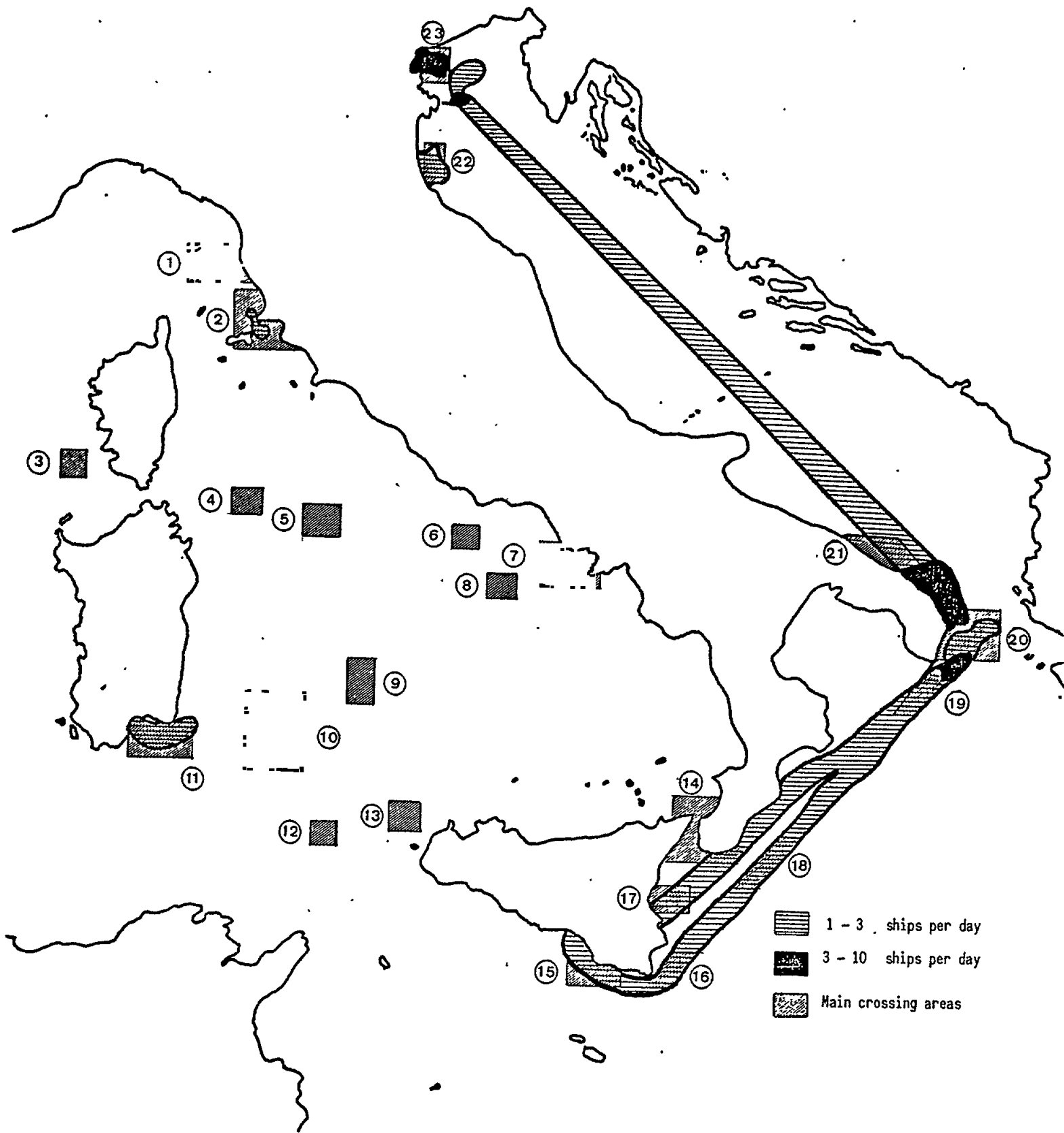
Map nr.5 - All Mediterranean identified routes calling at Italian ports in January and July 1982 (source COST 301 and CETENA)



Map nr.6 - Traffic density and main crossing areas in a sub-area all around Corsica  
(source COST 301)







Map nr. 8 - Main LNG-LPG traffic for Italian waters  
 (source COST 301)

tankers are Marsa-El-Brega/Cap Bon or Skida —> Marseilles or Barcelona or La Spezia, i.e. from the plants where the gas has been liquefied to the plants where it will be re-gasified.

For example, approximately 500 000 tons/years of butane and propane enter the port of Lavera (Marseilles) where they are stored in underground tanks ; about 200 000 tons are re-exported to Spain and Italy by coasters. For these two gases, 200 to 300 operations per year have taken place at Lavéra, an average of 1 ship per day. A total of approximately 2.7 million tons of LNG were imported from Algeria in 1983 by the Port of Marseilles (transportation is done by "Tellier" and "Hassi R'Mel" which both own a carrier of 40,000 m<sup>3</sup>.)

In the Italian waters, from 30 to 90 movements per month of LNG-LPG were recorded on the Adriatic coast, at the south of Italy, and off Sicily and Sardinia (map n° 8), with a maximal frequency (more than 90 movements per month) in the area of Venice and in the southern part of Italy between Otranto and Brindisi (studies done by the Italian Ship Research Center-CETENA).

Ammonia was among the products the most carried near the Suez and the Bosphorus.

Concerning other products listed in the IGC Code of the IMO, there is a large traffic of ethylene via Suez, from Marsa-El-Brega (Libya) and Marseilles \* (around 100,000 tons/year were exported) and of vinyl chloride, exported mainly from Marseilles-Fos (around 30,000 tons per year).

Other products having a low boiling point, are produced in the area Marseilles-Fos : propylene (500,000 tons/year) and chlorine (700,000 tons/year), but we do not have precise data concerning their traffic.

\* The ethylene pipeline between Marseilles and Lyon is the 2nd largest in Europe.

Let us keep in mind that in 1984 the world's fleet of gas carriers numbered 775, of which 36 were Greek tankers, 36 Italian tankers, 12 Spanish, 11 Russian and 9 were French.

#### 4.4. Maritime transportation of chemicals (other than liquefied gases)

Chemical transportation is done by two types of ships :

- those having a large capacity (about 40 000 tons) which carry either several types of chemicals (parcel tankers) or only one product (methanol, benzene, ethylene-glycol, phosphoric acid)
- those ships with a small capacity (about 3000 d.w.t.) which are essentially used in coastal trading ; more than 4/5 of the ships carrying chemicals in bulk are coasters.

It is to be noted that the world's fleet of chemical carriers was 847 units in 1984, of which about 40 were French, totaling about 1 million G.R.T.

The following table, extracted from a RIJKSWATERSTAAT Report gives some general information :

Average tanker capacity	4030 tons
Average capacity of a coaster	1500 tons
" " " " parcel tanker	15700 tons
Average number of tanks per ship	14
" " " " per coaster	12
" " " " per parcel tanker	23
Average quantity per tank	288 tons
" " " " for a coaster	125 tons
" " " " for a parcel tanker	683 tons
Average payload	77 %

Although the bulk transport of chemicals is fairly well studied for the English Channel or the North Sea, it is much less known for the Mediterranean unlike what is known for petroleum products and liquefied gases. The maritime transportation of



chemicals depends on their production and on their eventual use ; for products which are most often used, the producing countries tend to limit their dependence on other countries by producing the finished products such as PCV or polyethylene themselves.

General trends for Bulk chemical transport are obtained from statistics dealing with commercial exchanges by sea and especially from magazines such as "Maritime Transportation" and "Chemical Parcel Tankers", and from the French Journal of the Merchant Marine (see bibliography).

. The principal chemicals transported through the Suez Canal (coming from the Middle-East), with quantities greater than several hundred thousand tons per year are : benzene, ethanol, ethylene-glycol, hexane, methanol, sodium hydroxide, styrene, xylene.

. The principal chemicals leaving Marsa-El-Brega, where a large petrochemical complex is under construction at Ras Lanuf are : Ethylene-glycol, methanol, styrene.

- In Algeria, the facilities available at the petrochemical complex of Arzew which is currently being enlarged enable the exportation of : benzene, methanol, toluene, xylene (about 200 000 tons per year except for the methanol).
- Chemicals coming from Bulgaria, via the Bosphorus are : methanol and styrene.
- There is also a large coastal traffic of chemicals between the European Economic Community's countries ; about 200,000 tons of chemicals (1981) were exchanged between France and Italy, 100,000 tons between France and Spain, 100,000 tons between France and Greece.

In the Port of Marseilles-Fos, more than 400,000 tons (1986 data) of various organic chemicals were transported and twenty of these chemicals represented about 300,000 tons transported by about 250 ships (data from MAVRAC/Lavéra). Among the products most often carried : benzene, sodium hydroxide, ethyl-hexanol, butanol, monoethylene-glycol and chloroform (in decreasing order, for 1986 only).

As far as packed products are concerned, they are transported much less than bulk chemicals ; however, they are generally very toxic and the loss of containers which are swept over board during bad weather is frequent. A large diversity of products can be transported in a packaged form. A detailed list of these substances is given for the Marseilles-Fos Region in chapter 5. (table 3).

#### 4.5. Future traffic trends

A study by Holland's Maritime Economic Research Center-MERC (Hazardous Cargo Bulletin, Oct. 1986) dealing with deep-sea parcel tankers has noted an increase in traffic of 3-4 % per year between 1986-1990, with some nuances according to the nature of the chemicals.

The fleet of short-sea chemical parcel tankers will also probably increase. About 50 new deep-sea chemical parcel tankers will be built between 1986 and 1990. Transportation of organic chemicals (methanol, ethanol, xylene, styrene, and toluene) will increase by 10 % while that of inorganics (especially phosphoric acid, sodium hydroxide and sulfuric acid) will have a more stable transportation rate.

The implementation of Annex II of the 73/78 MARPOL Convention on April 6, 1987 will certainly have an impact on the development of new tankers and in particular their adaptation to new needs such as the recycling or the destruction of certain products of category A.

The trend will be towards a decrease of the old tanker fleet, which will greatly diminish the risks of marine casualties.

For natural gases, an increasing rate of 2 % is expected between 1982 and 1995 (Journal de la Marine Marchande, June 2, 1985) as apposed to 1% for petroleum.

Also, by 1990, gasoline in the industrial world will be virtually lead free which opens up possibilities for other octane

boosters such as methanol, benzene, xylene, toluene, ethanol, TBA, MTBE and TAME. \* (The acceptable amounts of these products which can be incorporated in gasoline has been defined by a Directive of the EEC Council (85/536) dated December 5, 1985).

Therefore, a large part of the traffic rate will concern antiknocks. For example, the traffic rate of boosters via the Suez Canal, by 1990, will be five times greater : about 4 million tons of Bulk chemical products, of which about 50 % will be methanol coming from Saudi-Arabia, will cross the Mediterranean.

This is one main reason why the ARCO chemical company is installed near Marseilles-Fos. This company plans to produce at the end of 1988, 430,000 tons/year of TBA, 180,000 T/year of propylene oxide and 50,000 T/year of propylene glycol.

Although it is beside the point of this study, it must be noted that river transportation of hazardous substances is also evolving. Thus, numerous bulk chemicals which come down the Rhone river carried by barges before being loaded in Fos, are at this time qualified as Class III chemicals, especially benzene. This river traffic will normally increase since benzene is one of the most frequently transported products (along with methanol) due to the "Shell Berre" company activities, in the Fos area.

## **5. CHEMICALS AND LIQUEFIED GASES IN MARSEILLES-FOS**

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Tables 1, 2 and 3 list respectively the liquefied gases (and low boiling point liquids from IMDG class III.1) which are loaded or unloaded in Marseilles-Fos, the bulk chemicals, and the chemicals which are transported in a packaged form at more than 10 tons per loading.

- \* TBA : Tertio Butylic Alcohol
- MTBE : Methyl-tertio-Butyl Ether
- TAME : Tertio-Amyl Methyl Ether

For each substance, these tables list the annual tonnage, the number of movements per year, and for tables 2 and 3, the age of the chemical tankers. These last two parameters are available only for chemicals inventoried in 1981. When possible we have used statistics from several years (for example 1981, 1984, 1986 and 70 days of 1984). In all cases the annual average was calculated by considering the periods of data collection which could be less than 1 year.

The information we used for the traffic of chemicals in the Port of Marseilles-Fos comes from several sources \* :

- CEDRE Report (R.83.775 R) dealing with statistics for 1981
- lists and data compiled by IFREMER, Toulon (1984, 85)
- MAVRAC, a company in Marseilles responsible for the administration of the chemical stocks (1986)
- DPNM, for the products most transported from 1982 to 1985
- telephone information from various sectors of the Port of Marseilles and the Company GAZOCEAN in Paris.
- CEPPOL, for the most recent data (the data collection is still underway on the basis of daily information sent by CECMED of the Maritime Prefect for the Third Region)

With all the chemicals and liquefied gases, the Port of Marseilles-Fos has an annual traffic of 5,250,000 tons. (This figure does not take into consideration the products which are transiting through the port). The traffic of liquefied gases is approximately 3,300,000 tons which is about 1,7 times that of the chemicals transported in bulk (1,900,000 tons) and is about 60 times that of the chemicals which are transported in a packaged form (50 000 tons).

\* See last page : "Glossary of abbreviations".

Table 1 : THE TOTAL AMOUNT OF LIQUEFIED GASES AND FLAMMABLE LIQUIDS CITED IN THE I.G.C. CODE AT MARSEILLE-FOS AND DETAILS OF SHIP MOVEMENTS

(Source : IFREMER and MAVRAC 1986)

LIQUEFIED GASES TO AND FROM MARSEILLE/FOS (ALL YEAR 1985) (IGC)	ANNUAL TONNAGE			TOTAL MOVEMENTS (per L.G.)	SHIP MOVEMENTS per L.G. and per TOWN or COUNTRY				Mean Tonnage per ship
	IMPORT	EXPORT	IMPORT + EXPORT		COMING FROM :		GOING TO :		
METHANE	2,385,796	-	2,385,796	137	SKIKDA : 115 ARZEW : 22				17,400
BUTANE	153,228	223,349	376,577	179	ARZEW : 5 SKIKDA : 5 YEMBO : 5  BARCELONA : 4 TARRAGONA : 4  RAS TANURA : 3 ZUEITINA : 2  FRA. ATLAN : 1 ISKENDERUN : 1 PORTSAID : 1		BASTIA : 27 AJACCIO : 11  TUNIS : 10 ALEXANDRIA : 9 BALEARES : 9 BIZERTE : 9  TANGER : 8 LUCIANA : 7  BARCELONA : 6 BEIRUT : 6 LEIXOES : 6  ALICANTE : 5 MOHAMMEDIA : 5 SFAX : 4	AGADIR : 3 CARTEGENA : 3 CORSICA AU : 3  CASABLANCA : 2 SPAIN : 2 FR. ATLAN : 2 HOUSTON : 2 LOBITO : 2 US GULF : 2  ANTWERP : 1 DAKAR : 1 DUNKERQUE : 1 LA NOUVELLE : 1 LARNACA : 1 LA VALETTE : 1 MALAGA : 1 NETHERLANDS : 1 RAVENNA : 1 ROTTERDAH : 1 SKIKDA : 1 TRIPOLI : 1	2,100
PROPANE	306,505	58,078	364,583	132	ARZEW : 16 SKIKDA : 10 HOUSTON : 7 YEMBO : 7  BARCELONA : 3 TARRAGONA : 2	ZUETINA : 2 FLUSHING : 1 ISKENDERUN : 1 LAKE CHARLES : 1 PORT SAID : 1 RASTANURA : 1	BASTIA : 15 TUNIS : 10 BIZERTE : 9 AJACCIO : 6 BEIRUT : 6 LEGHORN : 5 LUCIANA : 5 NAPLES : 5 ALEXANDRIA : 4 SFAX : 4 BARCELONA : 3 LEIXOES : 3	BALEARES : 2 CORSICA AU : 2 MOHAMMEDIA : 2 AGADIR : 1 CAGLIARI : 1 CARTEGENA : 1 FR. ATLAN : 1 LA NOUVELLE : 1 LARNACA : 1 LA VALETTE : 1 LISBON : 1 TRIPOLI : 1 VENEZUELA : 1	2,760
ETHYLENE	1,500	104,901	106,401	75	ARGENTINA : 1 SKIDA : 1		LEGHORN : 23 LYBIA : 17 NETHERLANDS : 16 BRINDISI : 5 MOHAMMEDIA : 3 ANTWERP : 2	PRIOLO : 2 TARRAGONA : 2 NORWAY : 1 PORTUGAL : 1 VADO LIG : 1 WILHEMSHAYEN : 1	1,420
VINYLCHELORIDE		31,270	31,270	13	LAKE CHARLES : 1		SALONIKI : 5 VENEZUELA : 2 AVEIRO : 1	KAOHSIUNG : 1 SPLIT : 1 YUGOSLAVIA : 1	2,405
BUTADIENE	12,491	3,069	15,560	9	BRAZIL : 2 PORTUGAL : 2	BRINDISI : 1	HOUSTON : 1 SALONIKI : 1	US GULF : 1	1,730
PROPYLENE		12,846	12,846	12			BRINDISI : 9 CAGLIARI : 2	ENGLAND : 2	1,040
DIISOBUTYLENE		4,495	4,495	3					1,500
ISOPROPYLAMINE			584	11					53
BROMOMETHANE			220	85					3
ETHYLETHER			57	2					29
ETHYLENE OXIDE			20	10					2
TOTAL	2,859,520	438,008	3,298,409	668					

LOADED AND UNLOADED BULK CHEMICALS AT MARSEILLES/FOS ( > 10 tons per movement)	ANNUAL TONNAGE					ANNUAL MOVEMENTS			AGE CLASSES FOR SHIPS (CEDRE)			MARPOL Cate- gory	HAZARD PROFILE (GESAMP)				
	CEDRE 1981	DPNM 1983-85	IFREMER 1984	MAVRAC 1986	MEAN	CEDRE 1981	MAVRAC 1986	IFREMER 1984	< 10 YEARS	10-20 YEARS	> 20 YEARS		A	B	C	D	E
	1 ACETIC ACID	6,714		57		5,604	59		100	36	7		16	C	0	2	1
ACETONE	44				44	3			2	-	1	C	0	0	0	0	0
ACRYLAMIDE	461				461	12			11	1	-	D	0	1	2	II	XX
ALKYL BENZENE		1,000			1,000							D	0	(0)	(0)	0	XX
AMMONIUM NITRATE	1,080		11,780		2,863	1		475	147	43	57	D	0	1	1	0	0
														DBO			
BENZENE	187,701	60,675		102,261	94,397	105	55					C	0	2	1	II	XXX
BUTYLACRYLATE	1,120		400		1,000	41		20	9	25	1	D	0	1	1	I	X
BUTYLENE GLYCOL		250			250							D	0	1	0	0	0
														DBO			
BUTYLMETHACRYLATE	104		160		113	6		10	5	-	-	(D)	0	1	0	I	X
10 CALCIUM HYPOCHLORITE	172		360		203	9		90	8	1	-	B	0	3	1	I	X
CHLORACETIC ACID	1,807				1,807	17			12	5	-	C	0	2	2	0	0
CHLOROFORM	2,933	8,070	420	9,964	7,152	21	10	30	18	2	-	B	2	2	2	1	XX
CHLOROSULFONIC ACID	212				212	5			2	2	-	C	0	2	1	I	0
CYCLOHEXANE	11				11	1			-	1	-	C	0	2	1	II	X
DIACETONE ALCOHOL	1,034		240		902	31		15	25	4	1	D	0	1	1	0	0
DICHLOROBENZENE	2,361		215		2,003	9		40	7	1	-	B	2	4	1	I	X
DICHLORO-1,2 ETHANE	157	4,930			3,737	4			3	1	-	B	2	1	2	II	XX
DICHLOROMETHANE	2,576	5,110	1,435	3,870	4,243	79	9	185	59	16	3	D	0	1	1	I	0
DICHLOROPHENOL	115		7,555		1,355	4		25	4	-	-	A	2	3	1	II	XX
20 DICYCLOPENTADIENE	11				11	1			1	-	-		0	0	2	0	0
DIETHYLHEXYL PHTHALATE					800		1					D	0	0	0	0	X
DIPENTENE	598		325		552	17		115	17	-	-	C	0	2	1	I	X
DIPROPYLENE GLYCOL				518	518		1						0	0	0	0	0
ETHANOL	15,642		1,640		13,308	22		395	12	10	-		0	0	0	0	0
ETHANOLAMINE	618				618	23			15	6	-	D	0	1	1	0	0
ETHYL HEXANOL	26,586			26,677	26,631	23		17	16	6	-	C	0	2	1	0	X
FERRIC CHLORIDE	19		165		43	1		40	1	-	-	C	0	2	1	0	X
FERROSILICON	19,517		10,330		17,986	36		490	34	2	-		-	-	-	-	-
FORMIC ACID	1,764		1,330		1,692	62		145	51	9	2	D	0	1	1	I	X
30 HEPTANOIC ACID	3,940	3,635			3,711	4			2	2	-	(D)	0	(1)	0	I	X
HYDROCHLORIC ACID	3,331		3,885		3,423	40		270	27	12	1	D	0	1	1	0	0
HYDROGEN PEROXIDE	9,465		11,560		9,814	136		295	110	23	3		0	2	0	0	0
ISOBUTYL ACETATE	53		170		73	3		35	3	-	-	C	0	2	1	I	0
ISOPROPANOL	489		100		424	22		95	14	8	-		0	0	1	0	0
MALEIC ANHYDRIDE	274		85		242	10		15	8	2	-	D	0	1	2	II	XX
METHANOL	2,329		160	12,871	6,924	17	6	140	12	4	1		0	0	1	0	0
METHYL ETHYL KETONE	3,915		15,370		5,824	47		160	31	10	6	D	0	0	1	0	0
METHYL ISOBUTYL KETONE	2,357		12,515		4,860	57		55	18	21	18	D	0	0	1	0	0
METHYL KETONE	329			5,241	2,785	5	11		4	1	-	D	0	0	1	0	0
40 MONOETHYLENE GLYCOL	2,897			10,559	6,728	5	10		1	4	-		0	0	1	0	0
MONOPROPYLENE GLYCOL	2,176			6,862	4,519	5	8		2	3	-		0	0	0	0	0
MORPHOLINE	161		235		173	7		20	6	1	-	D	0	1	1	I	0
N and ISO BUTANOL	20,843			11,647	16,245	44	16		32	8	-		0	1	1	0	0
NITRIC ACID	1,354		105		1,146	44		110	38	4	2	C	0	2	1	II	0
NITROMETHANE	489		15		410	13		20	3	10	-	(D)	0	(1)	1	I	X
OXALIC ACID	405				405	8			6	2	-	D	0	1	1	0	0
PARACRESOL	34				34	1			1	-	-	A	2	3	2	II	XX
PHENOL	6,610	4,930	30	8,046	5,664	17	10	40	3	12	2	B	+	2	2	II	XX
PHOSPHORIC ACID	259,041		170		215,896	134		120	96	33	2	D	0	1	1	I	0
50 PHOSPHORUS TRICHLORIDE	183				183	9			8	1	-	D	0	(1)	1	II	XX
POTASSIUM HYDROXIDE	1,931		795		1,741	74		250	44	22	4	C	0	2	1	I	0
PROPIONIC ACID	55				55	2			1	1	-	D	0	1	1	0	0
SODIUM HYDROXIDE			853 381		850,000			198	255	85	17	C	0	2	1	I	0
SODIUM NITRITE	2,575		1,185		2,343	67		185	59	7	1	B	0	3	2	0	0
SODIUM SULFIDE	1,830		555		1,617	36		40	28	5	3	(C)	0	3	2	II	XX
SULFUR	517,559		11,725		433,253	204		250	163	31	10		0	0	0	0	X
SULFURIC ACID	8,564		1,130		7,325	75		320	53	19	3	C	0	2	1	I	0
TETRACHLORETHYLENELEAD	4,361	5,470			5,192	70			44	21	5	B	2	3	0	0	X
TETRAETHYLLEAD	6,937		1,225		5,980	35		95	24	10	1	A	2	3	3	II	XXX
60 TITANIUM TETRACHLORIDE	361		50		351	9		10	2	-	-	D	0	2	2	II	XX
TOLUENE	14,875	1,235	435		4,445	57		105	32	22	3	C	0	2	1	I	X
TOLUENE DIISOCYANATE	5,869		8,600		6,324	137		250	75	39	5	C	0	2	0	II	XXX
TOLUIDINE	32		125		47	2		15	2	-	-	C	0	2	2	II	XX
TRICHLORETHANE			545		545			65	5	-	1	B	2	2	1	0	0
TRICHLORETHYLENE	1,123		685	2,235	1,589	47	6	165	37	8	2	B	2	2	1	II	XX
TRICHLOROBENZENE	1,483		1,210		1,437	37		75	31	6	-	B	2	(4)	1	0	X
TRIETHYLAMINE				298	298		1					C	0	2	1	I	X
TRIMETHYLAMINE	19				19	1			1	-	-	C	0	2	2	I	X
VINYL ACETATE	838		600		798	3		90	3	-	-	C	0	2	1	I	0
70 XYLENE	129,952	1,190	25		31,792	136		70	60	76	-	C	0	2	1	0	X

N.B : Data from IFREMER ou based on 70 days and extrapolated to 1 year by x 5.

Table 2 : THE TOTAL AMOUNT OF BULK CHEMICALS LOADED OR UNLOADED AT MARSEILLES-FOS, WITH NUMBER OF SHIP MOVEMENTS AND HAZARD PROFILES.

LOADED AND UNLOADED PACKED CHEMICALS  AT MARSEILLES/FOS ( > 10 tons per movement)	ANNUAL TONNAGE			ANNUAL MOVEMENTS		AGE CLASSES FOR SHIPS			HAZARD PROFILE (GESAMP)				
	CEDRE 1981	IFREMER 1984	MEAN	CEDRE 1981	IFREMER 1984	< 10 YEARS	10-20 YEARS	> 20 YEARS	A	B	C	D	E
	1 ACIPIC ACID	36		36	1		1	0	0				
AMMONIUM BIFLUORIDE	41	300	84	2	35	1	1	-					
ANHYDROUS ALUMINIUM CHLORIDE	9,965	1,740	8,652	21	20	9	5	4	0	1	1	0	X
ARSENIC	561		561	12		10	2	-	+	3	4	II	XXX
ARSENIC ACID	18		18	1		1	-	-	+	(3)	3	0	0
ARSENIC PENTOXIDE	34		34	2		1	1	-	+	(3)	3	0	0
ARSENIOUS ANHYDRIDE	4,873	3,600	4,661	92	150	41	50	1	+	3	2	II	XXX
BARYUM CHLORIDE		4,070	4,070	±	265								
BENZOYL PEROXIDE		125	125	15									
10 BUTYL GLYCOL	347		347	17		10	7	-					
BUTYL PHENOL	250		250	8		6	2	-	T	3	1	I	X
CADMIUM	43		43	1		1	-	-	+	4	2	II	XXX
CALCIUM CARBIDE	422	3,490	933	15	375	14	1	-					
CALCIUM SILICIDE		515	515		55								
CARBON DIOXIDE		240	240	85					0	2	-	II	XX
CARBON SULFIDE	359	1,070	447	2	60	2	-	-	(T)	2	3	I	XXX
CHLORACETYL CHLORIDE	385		385	11		8	2	-	0	2	2	0	X
CHLORODIFLUOROMETHANE		720	720		185								
CHROMIUM TRIOXIDE	85		85	2		2	-	-	Z	2	2	I	X
20 CYCLODODECATRIENE	48		48	2		1	1	-	0	3	1	II	XX
DICHLORODIFLUOROMETHANE		2,270	2,270		325								
D.D.T.	182		182	5		5	-	-	+	4	2	0	XXX
DICHLOROPHENYLISOCYANATE	65	170	82	1	10	1	-	-	-	-	-	II	XX
DIETHYL DICHLOROSILANE	11		11	1		1	-	-	0	1	1	II	XX
DIMETHOATE	1,528	310	1,325	19	35	14	4	1	0	4	3	1	XXX
DIMETHYL DICHLOROSILANE	51		51	4		2	2	-	0	1	1	II	XX
DIMETHYL ETHER ACETAMIDE	69		69	1		1	-	-					
DIMETHYLETHYLAMINE	305		305	15		11	3	-					
30 ETHYLCHLOROFORMATE	50		50	3		3	-	-	0	-	(3)	II	XXX
ETHYLGLYCOL	221		221	13	35	6	6	1	0	0	1	I	0
ETHYL GLYCOL ACETATE	315	335	318	15	40	9	5	1					
ETHYL HEXYL	11		11	1		-	1	-					
ETHYL-2 HEXYL CHLOROFORMATE		125	125		15								
ETHYL ORTHOFORMATE		75	75		20								
FORMOL	524	200	470	9	155	7	2	-	0	2	2	I	0
HEXAMETHYLENE TETRAMINE	131	1,145	350	6	85	6	-	-	0	0	0	0	0
HYDRAZINE		1,255	1,255		120				0	3	2	II	XXX
HYDROQUINONE		90	90		20								
40 ISOBUTYL CHLOROFORMATE	17		17	1		1	-	-					
LINDANE	178		178	7		7	-	-	+	4	2	0	XX
METALDEHYDE		45	45		20								
METHYLCARBONATE	54	320	98	3	30	3	-	-	0	-	(3)	II	XXX
METHYL CHLOROFORMATE	54	210	80	3	15	3	-	-	0	-	(3)	II	XXX
METHYL DICHLOROSILANE	51		51	4		2	2	-	0	1	1	II	XX
METHYL GLYCOL	21		21	1		1	-	-					
METHYL ISOCYANATE	15		15	1		1	-	-	0	-	2	II	XX
*METHYL-4 PENTANOL -2 (syn=methyl isobutyl carbinol)	99		99	6		1	3	-	0	1	1	I	0
NICKEL NITRATE		180	180		10								
50 NITROGEN PROTOXIDE		55	55		30								
OXYGEN		120	120		55								
PARADICHLOROBENZENE		95	95		15								
PARAFORMALDEHYDE		15	15		25								
PARAPHENITIDINE	368		368	17		17	-	-	0	(2)	(2)	II	XX
PARATHION	15		15	1		1	-	-	0	4	4	II	XXX
PHOSPHORIC ANHYDRIDE	325	90	286	16	10	11	3	-	0	1	1	I	0
PHOSPHORUS		690	690		45				+	4	4	II	XX
PHOSPHORUS PENTASULFIDE		25	25		10								
PHOSPHORUS PEROXIDE	80		80	1		1	-	-	+	4	4	II	XX
60 POTASSIUM NITRATE	148	25	127	5	35	2	2	1					
RESORCINOL		80	80		20								
SODIUM		130	130		20								
SODIUM ARSENITE	34	665	137	2	90	1	1	-	+	3	3	0	0
SODIUM BISULFATE	324	110	288	10	40	1	-	-	0	1	1	0	0
SODIUM CHLORATE	169	2,450	549	8	60	5	-	1					
SODIUM CHLORITE		530	530		40				0	2	3	I	0
SODIUM CYANIDE	3,095	310	2,631	58	50	42	11	5	0	4	3	I	0
SODIUM HYDROSULFITE	2,261	840	2,024	76	55	58	13	5	0	3	2	II	XX
SODIUM NITRATE		180	180		30								
70 SODIUM PENTACHLOROPHENATE	241	155	227	12	30	9	3	-	T	4	2	0	XX
THIOGLYCOLIC ACID	627	150	547	28	15	25	3	-	0	-	2	II	XX
THIONYL CHLORIDE	57	575	143	2	45	1	-	-	0	1	-	II	XX
TRIMETHYLACETYL CHLORIDE		475	475		65								
TRINITROTOLUENE	353	35	300	5	5	4	1	-	0	3	1	II	XXX
XYLIDINE	143	50	127	3	10	1	2	-	0	2	1	II	XX
76 ZINC PHOSPHIDE		50	50		5				+	3	3	II	XX

N.B : Data from IFREMER are based on 70 days and extrapolated to 1 year by x 5

Table 3 : THE TOTAL AMOUNT OF CHEMICALS - ON A PACKAGED FORM  
LOADED AND UNLOADED AT MARSEILLES-FOS, WITH NUMBER  
OF SHIP MOVEMENTS AND HAZARD PROFILES.

### 5.1. Liquefied gases

For the liquefied gases, the product the most often transported is methane with about 2.4 million tons, i.e. 70 % of the total liquefied gas traffic. The methane which is discharged in Fos comes exclusively from Algeria : from Arzew (22 movements/year) but especially from Skida (115 movements/year). The LNG is carried by methane tankers of approximately 40 000 tons, but the average tonnage which is discharged for each operation in Fos is 17 500 tons. If methane is the major product transported according to tonnage, it is the fourth most important in terms of number of movements : only 137 movements/year, as opposed to 311 for butane and propane, which is equal, in number of movements, to more than half the LG traffic.

The total tonnage of methane, butane and propane equals 95 % of the total liquefied gas traffic, and probably more if we consider the data of importation traffic from 1986 which are three times greater than that of 1985 (information from GAZOCEAN).

Other liquefied gases such as ethylene, vinyl choride, butadiene and propylene are less than 5 % of the tonnage, but equal 20 % of the movements.

### 5.2. Chemicals transported in bulk

The total tonnage of the inventoried products is about 1,850,000 tons. However, 80 % of the tonnage is covered by only three inorganic products : sodium hydroxide, sulfur and phosphoric acid. The first organic chemical, which arrives in 4<sup>th</sup> place, with a tonnage of about 100,000 tons/year is benzene. Table 4 which classifies in tonnage the bulk chemicals shows that :

- 3 products are carried at more than 100,000 tons/year.
- 7 products are carried at tonnages between 10,000 and 100,000 tons/year.
- 32 products are carried at tonnages between 1,000 and 10,000 tons/year.
- 18 products are carried at tonnages between 100 and 1,000 tons/year.



- 10 products are carried at less than 100 tons/year.

If we consider the classification of the same products by the number of voyages per year (table 5), the first places are filled by sulfur, sodium hydroxide, hydrogen peroxide, toluene diisocyanate and phosphoric acid with, respectively 212, 200, 162, 156 and 132 movements per year. The inorganic products are carried in large quantities, especially the products carried by specialized tankers (phosphoric acid tanker, for example).

### 5.3. Chemicals transported in a packaged form

Table 6 shows that :

- 9 products are carried at tonnages between 1,000 and 10,000 tons/year
- 39 products are carried at tonnages between 100 and 1,000 tons/year
- 33 products are carried at tonnages between 10 and 100 tons/year

Certain products, such as cyanide and arsenic compounds, are very often transported.

A classification of products which are transported more than 10 movements per year (less than 1 per month) is recapitulated in table 7. Five products are carried with a frequency rate higher than 100 ship movements per year ; these chemicals are : dichlorofluoromethane, barium chloride, chlorodifluoromethane, hydrazine and arsenious anhydride.

**Table 4 : MOST TRANSPORTED BULK CHEMICALS AT MARSEILLE-FOS  
BASED UP ON YEARLY TONNAGE.**

	LOADED AND UNLOADED CHEMICALS AT MARSEILLE/FOS BULK CHEMICALS > 1 000 T/ YEAR	ANNUAL TONNAGE
1	SODIUM HYDROXIDE	850,000
	SULFUR	433,250
	PHOSPHORIC ACID	215,900
	BENZENE	94,400
	XYLENE	31,790
	ETHYL HEXANOL	26,630
	FERROSILICON	17,990
	N and ISO - BUTANOL	16,245
	ETHANOL	13,310
10	HYDROGEN PEROXIDE	9,815
	SULFURIC ACID	7,325
	CHLOROFORM	7,150
	METHANOL	6,925
	MONO ETHYLENE GLYCOL	6,730
	TOLUENE DIISOCYANATE	6,325
	TETRAETHYLLEAD	5,980
	METHYLETHYL KETONE	5,825
	PHENOL	5,665
	ACETIC ACID	5,605
20	ETHYLENE TETRACHLORIDE	5,190
	METHYLISOBUTYLKETONE	4,860
	MONOPROPYLENE GLYCOL	4,520
	TOLUENE	4,445
	DICHLOROMETHANE	4,245
	DICHLORO.1,2 ETHANE	3,735
	HEPTANOIC ACID	3,710
	HYDROCHLORIC ACID	3,425
	AMMONIUM NITRATE	2,865
	METHYL KETONE	2,785
30	SODIUM NITRITE	2,345
	DICHLOROBENZENE	2,005
	CHLORACETIC ACID	1,805
	POTASSIUM HYDROXIDE	1,740
	FORMIC ACID	1,690
	SODIUM SULFIDE	1,615
	TRICHLORETHYLENE	1,590
	TRICHLOROBENZENE	1,435
	DICHLOROPHENOL	1,355
	NITRIC ACID	1,145
40	ALKYL BENZENE	1,000
	BUTYLACRYLATE	1,000

Table 5 : MOST TRANSPORTED BULK CHEMICALS AT MARSEILLE-FOS  
BASED UP ON YEARLY MOVEMENTS.

	LOADED AND UNLOADED CHEMICALS AT MARSEILLE/FOS BULK CHEMICALS e > 30 movements/ year	ANNUAL MOVEMENT
1	SULFUR	212
	SODIUM HYDROXIDE	200
	HYDROGEN PEROXIDE	162
	TOLUENE DIISOCYANATE	156
	PHOSPHORIC ACID	132
	XYLENE	125
	SULFURIC ACID	116
	FERROSILICON	112
	POTASSIUM HYDROXIDE	103
10	SODIUM NITRITE	87
	ETHANOL	84
	BENZENE	80
	AMMONIUM NITRATE	80
	HYDROCHLORIC ACID	78
	FORMIC ACID	76
	ETHYLENE TETRACHLORIDE	70
	METHYLETHYL KETONE	66
	ACETIC ACID	66
	TOLUENE	65
20	TRICHLORETHANE	65
	METHANOL	59
	DICHLOROMETHANE	57
	METHYLISOBUTYL KETONE	55
	NITRIC ACID	55
	TETRAETHYLLEAD	45
	TRICHLORO BENZENE	43
	TRICHLORETHYLENE	39
	SODIUM SULFIDE	37
	BUTYLACRYLATE	37
30	ISOPROPANOL	34
	DIPENTENE	33
	N AND ISO BUTANOL	30
	DIACETONE ALCOHOL	28
	CALCIUM HYPOCHLORITE	22
	CHLOROFORM	17
	VINYL ACETATE	17
	PHENOL	16
	DICHLOROBENZENE	14
	ISOBUTYLACETATE	8
40	FERRIC CHLORIDE	7

**Table 6 : MOST TRANSPORTED PACKED CHEMICALS AT MARSEILLE-FOS  
BASED UP ON YEARLY TONNAGE**

	LOADED AND UNLOADED CHEMICALS AT MARSEILLE/FOS PACKED CHEMICALS > 100 T/ YEAR	ANNUAL TONNAGE
1	ANHYDROUS ALUMINIUM CHLORIDE	8,640
	ARSENIOUS ANHYDRIDE	4,660
	BARIUM CHLORIDE	4,070
	SODIUM CYANIDE	2,630
	DICHLORODIFLUOROMETHANE	2,270
	SODIUM HYDROSULFITE	2,025
	DIMETHOATE	1,325
	HYDRAZINE	1,255
10	CALCIUM CARBIDE	935
	CHLORODIFLUOROMETHANE	720
	PHOSPHORUS	690
	ARSENIC	560
	SODIUM CHLORATE	550
	THIOGLYCOLIC ACID	545
	SODIUM CHLORITE	530
	CALCIUM SILICIDE	515
	TRIMETHYLACETYLCHLORIDE	475
	FORMOL	470
	CARBON SULFIDE	447
20	CHLORACETYL CHLORIDE	385
	PARAPHENITIDINE	370
	HEXAMETHYLENETETRAMINE	350
	BUTYL GLYCOL	345
	ETHYL GLYCOL ACETATE	320
	DIMETHYLETHYLAMINE	305
	TRINITROTOLUENE	300
	SODIUM BISULFATE	290
	PHOSPHORIC ANHYDRIDE	285
	BUTYL PHENOL	250
30	CARBON DIOXIDE	240
	SODIUM PENTACHLOROPHENATE	225
	ETHYL GLYCOL	220
	D.D.T.	180
	SODIUM NITRATE	180
	NICKEL NITRATE	180
	LINDANE	180
	THIONYL CHLORIDE	145
	SODIUM ARSENITE	135
	SODIUM	130
40	POTASSIUM NITRATE	125
	XYLIDINE	125
	ETHYL-2 HEXYL CHLOROFORMATE	125
	BENZOYL PEROXIDE	125
	OXYGEN	120
	METHYL-4 PENTANOL-2 (ISO butyl methyl carbinol)	100
	METHYL CARBONATE	100

**Table 7 : MOST TRANSPORTED PACKED CHEMICALS AT MARSEILLE-FOS  
BASED UP ON YEARLY MOVEMENTS.**

	LOADED AND UNLOADED CHEMICALS AT MARSEILLE/FOS PACKED CHEMICALS > 30 movements/ year	ANNUAL MOVEMENTS
1	DICHLORODIFLUOROMETHANE	325
	BARYUM CHLORIDE	265
	CHLORODIFLUOROMETHANE	185
	HYDRAZINE	120
	ARSENIOUS ANHYDRIDE	102
	CARBON DIOXIDE	85
	CALCIUM CARBIDE	75
	SODIUM HYDROSULFITE	72
	TRIMETHYLACETYL CHLORIDE	65
10	SODIUM CYANIDE	57
	CALCIUM SILICIDE	55
	OXYGEN	55
	THIONYL CHLORIDE	46
	PHOSPHORUS	45
	SODIUM CHLORIDE	40
	FORMOL	33
	NITROGEN PROTOXIDE	30
	SODIUM NITRATE	30
	THIOGLYCOLIC ACID	26
20	DIMETHOATE	22
	ANHYDROUS ALUMINIUM CHLORIDE	21
	HEXAMETHYLENE TETRAMINE	19
	ETHYL GLYCOLACETATE	19
	SODIUM CHLORATE	17
	ETHYL GLYCOL	17
	SODIUM ARSENITE	17
	SODIUM BISULFATE	15
	SODIUM PENTACHLOROPHENATE	15
	CARBON SULFIDE	12
30	POTASSIUM NITRATE	10

## 6. SHIP ACCIDENTS IN THE MEDITERRANEAN

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### 6.1. Localization of the Major Events at sea

Map n° 9, elaborated within the framework of the COST 301 program on the basis of data from the "Lloyd's Register Casualty Return", gives the localization of the principal casualties at sea all categories together, between 1976 and 1982. During this time, 280 accidents at sea were recorded which is an average of 40 per year.

If we take into consideration the data compiled by M.A.R.I.N (map n° 10) which include collisions, contacts, foundering and strandings (serious and non-serious cases), 305 casualties were recorded for a period of 5 years, i.e. 61 per year. Considering the annual ship traffic in the Mediterranean : 220,000 units (> 100 GRT), the casualty rate is about 0,03 % for the entire Mediterranean.

Among the areas of high occurrence of accidents :

- the eastern part of the Strait of Gibraltar and more precisely, a triangle Gibraltar - Cabo da Gata - Arzew, where trade routes coming from the north and south of the Mediterranean come together.
- a zone south-east of Greece and south of the Dardanelles which corresponds to the route followed by ships crossing the Bosphorus and traveling towards either Gibraltar or the North-Western Mediterranean.

In these two areas the number of casualties over the seven year period was approximately 30 for about 100 square miles, i.e. more than 4 casualties per year.

Other zones show a large number of casualties :

- a line running along the African coast (except in the Gulf of Sidra) which corresponds to the trade route Suez-Gibraltar.
- in the very eastern Mediterranean and around Cyprus.

In other areas casualties are more scattered ; however, some zones are more densely accidented : around Sicily, south of Sardinia, north of Corsica, south of Barcelona-Tarragone. The white areas on the map are zones which are less ship traveled. Map n° 10 also exposes the navigation problems related to the islands in the Aegean sea (generally "serious casualties").

For each Mediterranean sub-area of the COST 301, M.A.R.I.N. is able to furnish case studies dealing with :

- the size of the vessel in GRT (7 classifications) ;
  - the type of ship (18 classifications) including LNG, LPG and chemical tankers ;
  - The casualty categories (5 classifications) ; each class is divided into sub-classes, for example for "collision" : 3 defined types in function of the angle of coincidence (meeting, overtaking, crossing) ;
  - date of casualty ;
  - lives lost ;
  - pollution ;
  - ship particularities (7 classifications) ;
  - weather (13 classifications) ;
- and other details.

We have not been able to obtain these data in time for an in-depth interpretation ; however, as an example, we expose the case of a sub-area which illustrates the data (taken from COST 301

Report entitled "Marine traffic casualties in the COST 301 area 1978-1982 - Final Report on Contract EUR-NM-013.NL"). For the sub-area n° 152 (Bosporus-Dardanelles) : 1 head-on collision of a chemical tanker (1600-10 000 G.R.T.) and 2 wrecked/stranded ships a chemical tanker and a LPG tanker (same classes of GRT).

#### 6.2. Accident Case studies for ships transporting hazardous substances

Among the principal cases of hazardous materials (HM) spilled at sea, we can distinguish :

- accidents at sea or along the coastline.
- accidents at stationary plants (related to the loading/unloading).
- operational spills related to tank cleaning
- chemical dumping at sea

Only the first point is covered here.

The most well-known accidents involving hazardous substances in the Mediterranean are :

#### - for liquefied gas tankers

. the "EL PASO PAUL KAYSER" during a manoeuver to avoid a collision, sunk near Gibraltar on a rocky sea floor (1980). The loaded tanker's hull was torn open, but no tank rupture was observed and consequently no spillage was registered. The oil transfer was accomplished under good conditions to the "EL PASO SONATRACH".

. The "GAS EAST", Greek butane tanker, in the harbour of Hyères, heeled over, probably due to an error in the cargo loading (lack of stability). It was destroyed at sea by the French Navy.

. the "GAS FOUNTAIN", carrying 15 600 tons of butane and 7,800 tons of propane : due to a fire in the machine room the tanker was found in the Mediterranean with no means of propulsion.



The ship towed to Fos, and its cargo was transferred to the tanker "GARALA".

. the LPG-tanker "BRIGITTA MONTANARI" accident in the Adriatic Sea (Nov. 1984). The 1 300 GRT cargo Sunk ; only small amounts of fuel-oil spillage was noted.

- for chemical tankers :

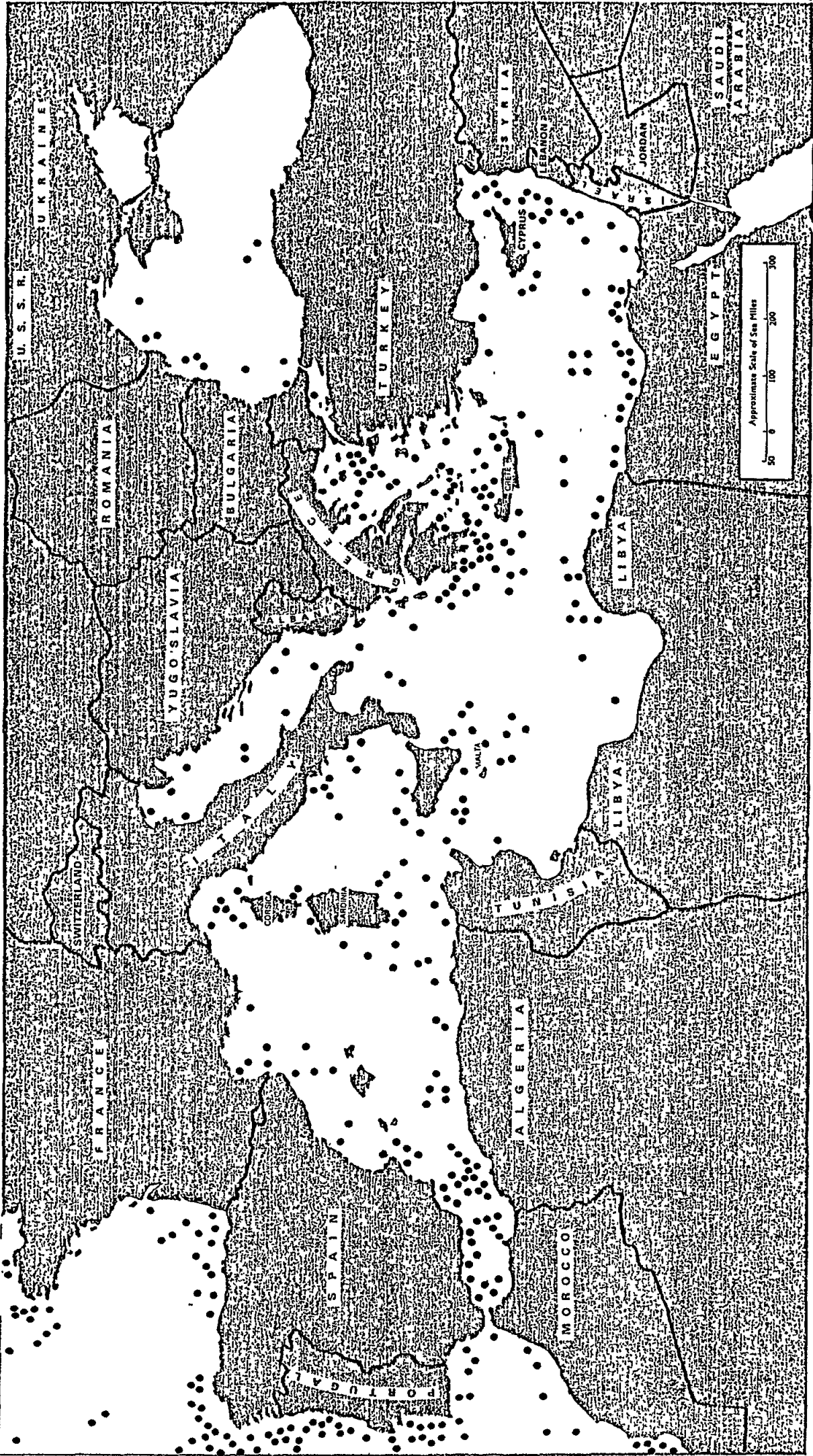
. The KNOHR BURCHARD, at Livorno (Italy) where a large styrene spill occurred.

- for packed-chemical carriers :

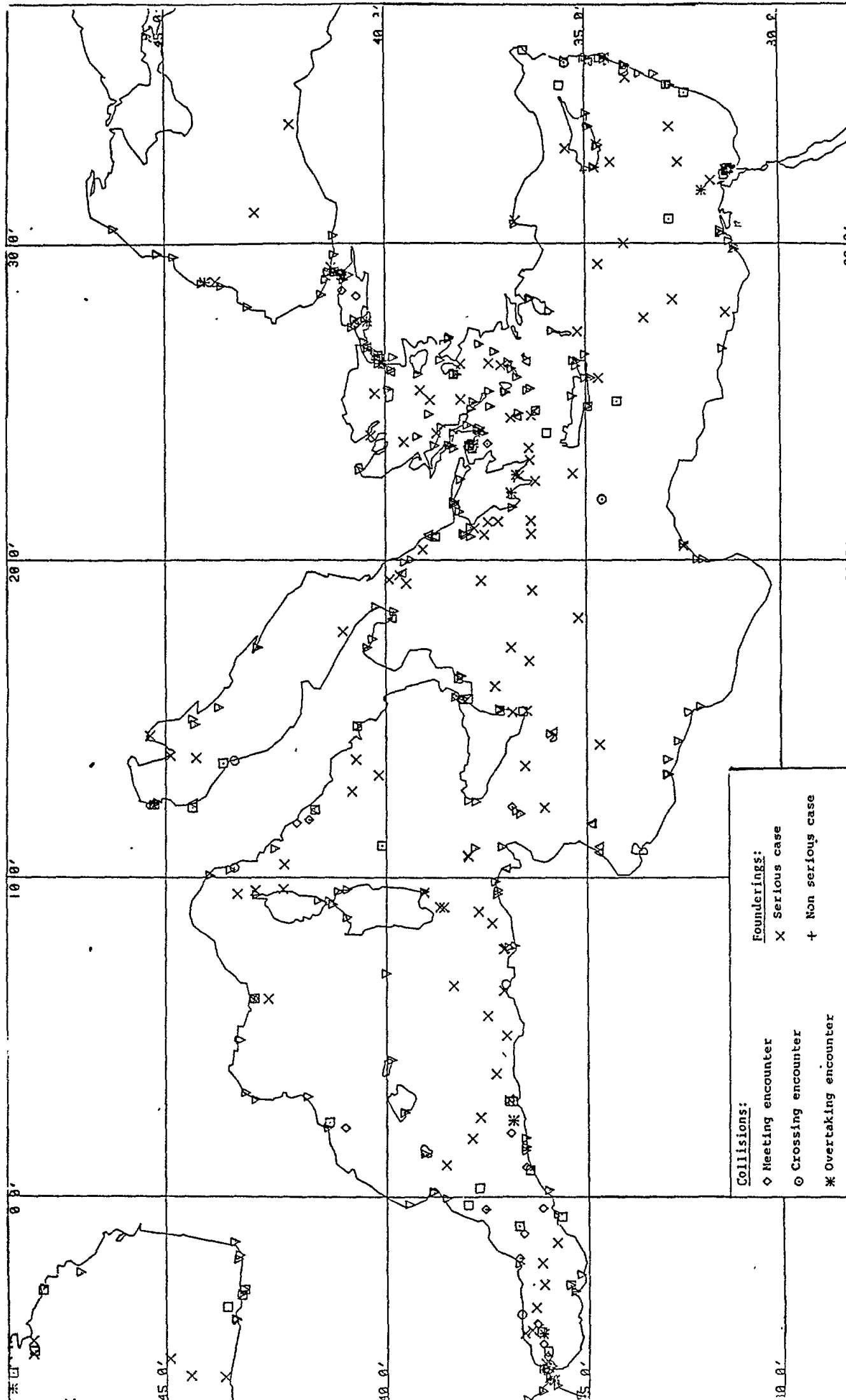
. 900 drums of lead antiknock fell off the Yugoslavian freighter "CAVTAT" in the Strait of Otranto (S.E. Italian coast) on July 14, 1974. The cargo contained 150 tons of tetramethyl lead and 120 tons of tetraethyl lead. On 22 april 1978, 872 drums were recovered. A lack of 21.5 tons was notified (IMO, 1979).


2 papers presented in 1977 at Rovinj, Yugoslavia, deal with lead alkyls behaviour in the marine environment (see bibliography). They present methods available for calculating the dispersion of lead alkyls released from a source on the sea-bed. For conditions likely to exist in the Strait of Otranto, it is estimated that safe concentrations of TML and TEL will be reached well within a few hundred meters from a source located on the sea-bed. Concerning the risk caused in the marine environment, it has been demonstrated that the toxicity of alkyl lead compounds is directly related to the degree of alkylation and to a lesser extent to the nature of the alkyl groups. Safe levels for tri-alkyl lead chlorides (the first degradation step for tetra alkyl forms) have been calculated between 1 p.p.b and 0.1 p.p.m.

The major environmental impact of a release of tetra alkyl lead compounds into the marine environment is more likely to be due to acutely toxic effects than those of bioaccumulation.



Map nr. 9 - Summary chart of casualty data in the Mediterranean Sea (1976-82) from Lloyd's Register Casualty return (in Mediterranean Report to COST 301 C.S.T.)





**DANISH MARITIME INSTITUTE**  
LYNGBY DENMARK

MEDITERRANEAN CASUALTIES 1978-82

ORDER 8537 DATE 8505

<b>Collisions:</b>	<b>Founderings:</b>
◇ Meeting encounter	X Serious case
○ Crossing encounter	+ Non serious case
* Overtaking encounter	
□ Unknown type	
<b>Contacts:</b>	<b>Standings:</b>
▣ Serious case	▽ Serious case
▤ Non serious case	△ Non serious case

Map n°10: Mediterranean casualties 1978-1982  
(source: DMT/COST 3011)

. The same day, but five years later, July 14, 1979, the Greek freighter "KLEARCHOS" heeled over outside the port of Olbia (Sardinia) with various chemical products including metal drums containing arsenic compounds.

. the "SUNNY KARINA", a dry cargo freighter, lost containers of ethyl acrylate and titanium dioxide (March, 1981) near Cape Bon, Tunisia.

. The "VICKY B", a general cargo ship, lost its cargo of chemical substances (February, 1984).

The characteristics of three of these accidents along with their trees of events are presented in Annex VI.

On January 11, 1987, the French Ro-Ro "Cap Ferrat" lost 2 protected tanks (6 x 2.4 m) each containing 19 tons of tetraethyl lead off Barcelona, at around 1500 m. deep. The cargo was probably dislocated during the sinking and the tetraethyl lead will no doubt remain in a localised zone. Slow degradation in tri, di, monoethyl oxide and inorganic lead do not seem to affect marine life.

Historical accidents concerning collisions, strandings, hull and machinery incidents involving ships used for the transport of liquefied gases, and Fire/explosion incidents that have occurred on the same carriers were examined by Blything and Lewis (1985) and Blything and Edmonson (1984).

### 6.3 The risks of accidents (for the whole Mediterranean)

In 1984 approximately 2.7 % of the world's fleet of ships specialized in transporting dangerous substances, equal to 31 ships out of 847, were involved in serious accidents. Of these 31 vessels, there were 4 explosions or fires, 3 collisions, six groundings and 18 accidents for diverse reasons (running into a dock, etc.).

In terms of a percentage of chemical/gas carriers' casualties compared to oil tankers' casualties, the chemical carriers presented the highest accident rate, as shown in the table below ; taken from the "Tanker Casualty Bulletin".

SHIP TYPE	Ships at risk	TANKER CASUALTY 1984		SERIOUS TANKER CASUALTY (1984)	
		N°	%	N°	%
Oil tankers	6,647	583	8.8	133	2.00
Combination carriers	400	93	23.3	11	2.75
Chemical carriers	847	131	15.5	31	3.66
Gas carriers	775	80	10.3	13	1.68

Table 13, involed in the Annex, gives the casualties which occurred in the Mediterranean during 1985 (source : Lloyds Register of Shipping, 1985).

Lloyds' statistics for 1985 (table 13) showed that for Mediterranean, 31 losses and 23 casualties, divided in the following casualty categories have, occurred :

Casualty category	Losses	Casualties	Total
Foundered	10	2	12
Fire/Explosion	7	7	14
Collision	3	1	4
Contact	1	0	1
Wrecked/Stranded	7	10	17
War/hostilities	3	2	5
Miscellaneous	0	1	1
Total	31	23	54

Among the 54 vessels which suffered casualties (for the Mediterranean, Lloyds' data 1985) ;

- . 37 General Cargos
- . 4 Tankers
- . 3 Fishing
- . 2 Bulk carriers
- . 2 Ferries
- . 1 Container Ships
- . 1 L.G. Carrier
- . 1 Ro-Ro
- . 1 Supply Ship

Considering hazardous cargo, the LPG "Brigitta Montanari" which foundered on November 1984 but was cited on the Lloyds' list for 1985, is, with no doubt, the most serious casualty for hazardous materials. Tankers transporting fuel or gasoline can cause a release of hazardous substances. But many "general cargoes" (with or without containers), have no specifications concerning their loads.

A study by the Canadian Coast Guard, covering the years 1969 to 1972, showed that - for LNG carriers - of 4337 movements, no cargo spillage occurred ; however there were 6 groundings, 4 collisions or contacts and 4 serious impacts.

In the Mediterranean, for an annual traffic of about 220,000 units, the number of accidents (all ships > 100 GRT) is about 60 per year, i.e. a likelihood of accident for every 1 out of 3700 ships or about 0.03 %. This average is comparable to that of the Dutch territorial waters (0.02 %).

If we consider that 1/6 of the world's fleet of specialized carriers. (i.e. : 140 chemical tankers) travel through the Mediterranean, and also, that 3.7% of the world's serious accidents involve this type of tanker, we can conclude that an average of 5 chemical carriers per year will have accidents in the Mediterranean.

The same logic can be applied to liquefied gas carriers which will give the figure of 2 accidents per year.

If we add the fleet of combination carriers and tankers carrying packed chemicals, we can estimate the number of accidents for ships transporting hazardous substances within the Mediterranean sea to be about ten per year. However statistics for 1985 (table 13) show that only 1 LG tanker was involved in a casualty in the Mediterranean and no chemical carriers. Only general cargos were able to transport HM, but we do not know their nature.

TABLE 13 :  
 (source : Casualty Return, 1985 - Lloyd's Register of Shipping)  
**Details of total losses during 1985 FOR THE MEDITERRANEAN SEA**

(Listed in alphabetical order of ship name within casualty category.)

### Foundered

Ship's name and year of build	Gross Tonnage	Flag	Type	Voyage	Cargo	Circumstances and place	Date
AL HADI 1964	1 183	LEB	m General Cargo	Chalkis—Sudan	general	4 miles off Porto Rafti, Greece, after cargo shifted.	3 Oct
GLORIA I 1952	399	CYP	m General Cargo	Beirut—Limassol	..	Sprang leak in engine room and sank 9 miles N.W. of Beirut.	10 Aug
JUSANT 1959	139	ALG	wm Fishing Side Trawler	..	..	Sprang leak and presumed to have foundered 50 miles S.W. of Almeria.	2 Jan
KOSTIS M 1961	397	GRC	m General Cargo	Santorini Island—Piræus	pumice	3 miles S. of Ios Island, Greece.	4 Mar
KRITI 1957	481	GRC	m General Cargo	Nisiros Island—Iraklion	pumice	Presumed to have foundered off Crete in heavy weather.	20 Oct
LUCKY STAR 1959	398	CYP	m General Cargo	Alexandria—Beirut	potatoes & artichokes	At Alexandria outer anchorage, in lat. 31 11 30N., long. 29 47 00E., whilst in tow after sustaining main engine breakdown.	7 Feb
MARIOS M 1956	995	HON	m General Cargo	Rhodes—Lebanon	..	Off Cyprus, in lat. 36 00N., long. 32 32E.	28 Apr
SINNO M. E. 1964	1 718	LEB	m General Cargo/ Vehicles Carrier	Barcelona—Beirut	containers & PVC chips	1 mile off Barcelona, after developing list.	28 Jun
TIM STAR 1976	493	EGY	m Tug/Supply Ship Deck Cargo	at Alexandria	..	Capsized and sank at Alexandria, in lat. 31 09 48N., long. 29 48 58E., in heavy weather.	17 Jan
VADI 1969	396	TRK	m General Cargo	Bandirma, Turkey—Erdek, Turkey	pyrites	1½ miles W. of Marmara Island.	12 Dec

### Fire/Explosion

Ship's name and year of build	Gross Tonnage	Flag	Type	Voyage	Cargo	Circumstances and place	Date
ANADOLUKAVAGI 1961	781	TRK	m Ferry	at Karakoy	..	Extensively damaged by fire at Karakoy, Istanbul; subsequently beached, refloated, taken to Istinye and sold for breaking up.	5 Mar
CAMPONAVIA 1973	4 222	SPN	m Tanker	at San Roque Terminal	gasoline	Sank after explosion and fire whilst loading at San Roque Terminal, Algeciras Bay; subsequently raised, sold and broken up.	26 May
ELEFTHERIA M 1965	38 275	LIB	m Tanker	at Porto Marghera	fuel oil	Extensively damaged by fire in accommodation whilst discharging at Porto Marghera; subsequently towed to Barcelona, sold and broken up.	1 Apr
HARIS 1972	3 621	CYP	m Container Ship Fixed-guides	Limassol—Algiers	..	Extensively damaged by fire in engine room in lat. 36 49 00N., long. 01 47 30E., and anchored off Algiers; subsequently towed to Cartagena, Spain, sold and broken up.	15 Feb
MAREL 1969	9 853	CYP	m Bulk Carrier	Thessaloniki—Belgium	..	Sank after explosion and fire in engine room off Cabo de Gata, Spain.	14 Nov
ODEA 1970	3 298	CYP	m General Cargo	Demerara—Greenock	sugar & empty containers	Caught fire in accommodation in lat. 35 53N., long. 28 29W., and towed to Ponta Delgada; subsequently towed to Greenock and thence to San Esteban de Pravia, sold and broken up.	3 Oct



## Fire/Explosion

Ship's name and year of build	Gross Tonnage	Flag	Type	Voyage	Cargo	Circumstances and place	Date
SELENE ARA 1975	1 559	ITL	m Tanker	Civitavecchia— Adriatic Sea	..	Extensively damaged by explosion and fire 40 miles W. of Naples and sank off Gaeta Roads, in lat. 41 11 42N., long. 13 37 12E., whilst in tow in heavy weather.	6 Aug

## Collision

Ship's name and year of build	Gross Tonnage	Flag	Type	Voyage	Cargo	Circumstances and place	Date
AGIP MUREX 1982	1 096	ITL	m Supply Ship Deck Cargo	Siracusa— ..	supplies	Sank after collision with ALHAMBRA 12 miles S.W. of Capo San Marco, in lat. 37 20N., long. 12 54E., in dense fog.	24 Aug
MARIA MONICA 1969	1 598	ITL	m General Cargo	Alexandria— ..	..	Sank after collision with UNI-FORTUNE off Crete, in lat. 33 35N., long. 27 30E.	12 Jan
ROSA GANCITANO 1970	146	ITL	wm Fishing Side Trawler	..	..	Sank after collision with TODARO 25 miles W. of Lampedusa, Italy.	4 Aug

## Contact

Ship's name and year of build	Gross Tonnage	Flag	Type	Voyage	Cargo	Circumstances and place	Date
KIBRIS I 1961	293	TRK	m RoRo Cargo/Ferry Deck Cargo	at Morphou Bay	..	Struck jetty at Morphou Bay in heavy weather; subsequently sank on 5 February.	4 Feb

## Wrecked/Stranded

Ship's name and year of build	Gross Tonnage	Flag	Type	Voyage	Cargo	Circumstances and place	Date
BRAVO 2 1947	371	PAN	m General Cargo	at Limassol	..	Stranded at Limassol in heavy weather, whilst laid up; subsequently refloated and broken up.	18 Jan
GIORGIONE 1962	20 841	GIB	m Tanker	.. —Melilli	..	Stranded on rocks at Santa Panagia Bay, in lat. 31 06 25N., long. 15 17 22E., after moorings parted in heavy weather; subsequently refloated, towed to Algeciras, sold and broken up.	17 Jan
KAZAR 1966	399	LEB	m General Cargo	at Jounieh	..	Stranded in Jounieh Bay after dragging anchors in heavy weather; subsequently refloated, sold and broken up in situ.	5 Feb
LINA 1955	485	HON	m General Cargo	Limassol—Alexandria	bentonite, whisky & general	Developed list in lat. 33 40N., long. 34 10E., in heavy weather; subsequently stranded and broke in two 15 miles N. of Beirut on 21 February.	14 Feb
MAIORCA 1962	498	ITL	m General Cargo	Porto Empedocle— Baia	..	Stranded on rocks off Capo Miseno, Baia; subsequently refloated, taken to Baia, beached and sold for breaking up.	27 Feb
MANJEE MOON 1969	2 867	MTA	m General Cargo	Setubal—Karachi	general	Stranded off Punta Leona, in lat. 35 56N., long. 05 24W., after main gear shaft broke; subsequently refloated and towed to Ceuta, sold and towed to Cadiz for breaking up.	18 Jul
MILAS 1970	3 999	TRK	m General Cargo	..	..	Stranded off Elafonisos Island, S.W. Peloponnisos, in lat. 36 29N., long. 23 00E., in heavy weather; subsequently refloated, renamed NEAPOLIS, taken to Perama, sold and broken up.	17 Jan

Lost, etc.,  
 .(i) War Loss/Damage During Hostilities

Ship's name and year of build	Gross Tonnage	Flag	Type	Voyage	Cargo	Circumstances and place	Date
ADEL 1959	495	LEB	m General Cargo	at Tripoli, Lebanon	..	Sunk during hostilities at Tripoli, Lebanon.	9 Oct
ATTAVIROS 1960	493	PAN	m General Cargo	..	..	Sunk during hostilities 100 miles off Israel.	20 Apr
SEADOLL 2 1968	1 596	CYP	m General Cargo/ Container Ship Fixed-guides	Beirut— ..	..	Sank 20 miles off Beirut after mine explosion.	12 Sep

## Additional information (casualty)

This section contains recently reported total losses occurring prior to 1985.

### Foundered

Ship's name and year of build	Gross Tonnage	Flag	Type	Circumstances, place and date
AL TAIF 1949	5 284	SAU	m Passenger/General Cargo/Ferry	Reported foundered in Suez Roads on 15 January, 1981.
BRIGITTA MONTANARI 1970	1 297	ITL	m Liquefied Gas Carrier LPG	Reported foundered off Sibenik, in lat. 43 42 54N., long. 15 33 48E., on 16 November, 1984, after developing list.

### Fire/Explosion

Ship's name and year of build	Gross Tonnage	Flag	Type	Circumstances, place and date
ATLAS V 1983	724	PAN	m Factory Fishing Fish-factory	Reported damaged by fire in lat. 39 15N., long. 12 14E., on 18 September, 1982, and taken to Naples; subsequently broken up.
AZIZ 1953	1 365	LEB	m General Cargo	Reported extensively damaged by fire in engine room and accommodation in Beirut Roads on 26 February, 1983, in heavy weather and towed into port; subsequently towed to Limassol and broken up.
EVANTHIA I 1962	499	CYP	m General Cargo	Reported extensively damaged by explosion and fire off Ancona, in lat. 43 22N., long. 14 22E., on 18 November, 1984; subsequently towed to Ortona and sold for breaking up.
FOLLO 1968	965	NOR	m General Cargo	Reported extensively damaged by fire in engine room off Algeria, in lat. 38 25N., long. 07 45E., on 2 December, 1980 and towed to Cagliari; subsequently towed to Savona and broken up.
GIANNAKIS 1958	2 624	GRC	m General Cargo	Reported extensively damaged by explosion and fire in engine room off Kos, in lat. 36 47N., long. 27 17E., on 1 March, 1983, towed to Amorgos Island and beached the following day; subsequently refloated, towed to Piræus and broken up.
GONGOLA 1971	3 002	GRC	m General Cargo	Reported extensively damaged by fire in engine room and accommodation S. of Crete, in lat. 34 40N., long. 27 00E., on 29 December, 1982; subsequently towed to Piræus, sold and broken up.
REA 1961	4 125	GRC	m General Cargo	Reported extensively damaged by fire in accommodation at Bejaa on 18 December, 1982 whilst discharging cargo, subsequently towed to Piræus and thence to Aspropyrgos, sold and broken up.

### Collision

Ship's name and year of build	Gross Tonnage	Flag	Type	Circumstances, place and date
PROMITHEUS 1966	22 593	PAN	m Bulk Carrier	Reported beached after collision with GARBIS and PASADENA in Aliveri Bay on 2 March, 1984; subsequently refloated, towed to Chalkis and thence Piræus and sold for breaking up.

## Wrecked/Stranded

Ship's name and year of build	Gross Tonnage	Flag	Type	Circumstances, place and date
IOANNIS M. 1962	497	GRC	m General Cargo	Reported stranded and sank off Greece, in lat. 38 05 36N., long. 24 35 00E., on 29 July, 1984, in heavy weather.
KVARNER 1946	3 185	YUG	m General Cargo Ref	Reported damaged by stranding off Durres on 21 May, 1984, refloated, taken to Cres and laid up; subsequently taken to Split, sold and broken up.
LAMBROS 1963	2 753	GRC	m General Cargo	Reported stranded off Porto Palo, Sicily on 22 September, 1984; subsequently refloated, towed to Palermo, sold and broken up.
M. HARB 1956	849	LEB	m General Cargo	Reported wrecked on breakwater at Limassol on 9 March, 1984, after dragging anchor in heavy weather.
MARITASIA 1962	778	CYP	m General Cargo	Reported stranded off Ios, Greece on 11 July, 1984; subsequently refloated, towed to Piræus, sold and broken up.
NAVICO 1955	1 253	LEB	m General Cargo	Reported stranded off Symi island on 17 November, 1982, after engine trouble in heavy weather, refloated and towed to Rhodes and thence to Perama; subsequently taken to Beirut and thence to Piræus, sold and broken up.
ORINOCO 1962	115	PAN	m Tug	Reported wrecked between Alexandria and Port Said on 14 May, 1980.
PHILLIP 1966	7 948	PAN	m General Cargo	Reported stranded off Laurium on 9 August, 1984, after sustaining rudder trouble; subsequently refloated and taken to port, towed to Piræus and thence to Gadaní Beach and sold for breaking up.
POSEIDON C 1956	3 611	PAN	m General Cargo Ref	Reported developed list and beached at Katakolo on 26 July, 1979; subsequently refloated, taken to Eleusis, sold and broken up.
THIA DESPINA 1948	11 276	CYP	m General Cargo Ref	Reported stranded off Port Said on 9 July, 1977, refloated, taken to Piræus and laid up; subsequently taken to Aliaga, sold and broken up.

## Lost, etc.

### (i) War Loss/Damage During Hostilities

Ship's name and year of build	Gross Tonnage	Flag	Type	Circumstances, place and date
MY CHARM 1960	537	CYP	m General Cargo	Reported damaged during hostilities at Tripoli, Lebanon, on 18 December, 1983; subsequently towed to Limassol, sold and broken up.
CHOUKRI 1958	361	LEB	m General Cargo	Reported struck by missile and sank at Beirut on 26 August, 1984.

### (iii) Miscellaneous

Ship's name and year of build	Gross Tonnage	Flag	Type	Circumstances, place and date
MARO 1923	142	CYP	m General Cargo	Reported lost off Lebanon in 1981.

- The age of the vessels is a well-known risk factor, and the likelihood of marine casualties will increase with an increase in shipage.

The "guide on Maritime Transportation" - relying on data from 1982 for the French merchant fleet- mentions that :

- of 7 liquefied gas tankers, 1 is older than 10 years and 1 is older than 15 years.
- of 9 chemical tankers, 1 is older than 20 years and 1 is older than 25 years.

Data collected for chemicals loaded or discharged in Marseilles-Fos during 1981 enabled us to elaborate Table 8 where the chemicals are classified by the age of the carriers, notably the classification of 10-20 years and that of more than 20 years. The overall data (for 1981) is presented in Table 13

Only one product was carried by old vessels : ammonium nitrate which was carried (in 1981) on 57 voyages by ships more than 20 years old, and on 43 voyages by ships between 10 and 20 years old. (Ammonium nitrate is carried by small bulk carriers or by dry cargos and presents a risk of explosion when exposed to heat from a fire.)

The risk of accidents due to shipping of chemicals by old carriers is low : only 4 other chemicals are carried at a frequency of 10 to 20 movements per year by ships older than 20 years.

Sodium hydroxide has been transported on 85 voyages by 10 to 20 year old vessels. Xylene and arsenious anhydride have an annual movement of 76 and 51 voyages respectively by ships more than 10 years old. However, for the majority of chemicals listed in Table 9, containing a large number of toxic chemicals transported in packages, most of the transportation is done by ships which are less than 10 years old.(data for 1981).

#### 6.4. Risks of accident (for ships coming into or out of the Port of Marseilles-Fos).

On the basis of the Casualty Risk Assessment proposed in the preceding section (6.3), which is 0.03 % for the entire Mediterranean, we can estimate - on the basis of the frequency of chemical transport - the probability of an accident which could involve a chemical spill during a given period.

This estimation makes three assumptions :

- The risk of marine casualty, calculated from data dealing with all the traffic, is applicable to tankers carrying liquefied gases and chemicals.

- The risk of ship accidents involving hazardous substances is only applicable for ships using the trade routes to and from the Port of Marseilles-Fos.

- The risk of release of a chemical, in the case of a bulk transportation, depends on the type of the chemical carrier (I, II or III of IBC Code for example).

In order to extrapolate the frequency of chemical traffic in all the Mediterranean, we must have precise data regarding chemical movements per year, especially through the Suez Canal and the Strait of Gibraltar, which is not the case.

Table 9 is therefore based on the number of voyages for each type of chemical. Thus, for liquified gases, the risk of an accident involving a carrier transporting butane is 1 every 21 years ; for methane, 1 accident is probable every 27 years ; for propane, one every 28 years. For all liquefied gases and volatile liquids (listed in the IGC Code), the accident probability is one LNG-LPG carrier approximately every 5 years. Using the same logic, the probability of an accident for Bulk chemical carriers (parcel tankers and coasters) is on the order of 1 accident every 1.2

TABLE 6 : MOST TRANSPORTED CHEMICALS (BULK + PACKAGED FORM)  
 BY > 20 YEARS AND 10-20 YEARS OLD CARRIERS  
 (STOPPING AT MARSEILLE-FOS)

B : Bulk P : Packaged form	LOADED AND UNLOADED CHEMICALS AT MARSEILLES/FOS	AGE CLASSES FOR SHIPS in 1981		ANNUAL TONNAGE
		>20 YEARS	10-20 YEARS	
		B	AMMONIUM NITRATE	
B	METHYLISOBUTYL KETONE	18	21	4,860
B	SODIUM HYDROXIDE	17	65	850,000
B	ACETIC ACID	16	7	5,605
B	SULFUR	10	31	433,250
B	METHYLETHYL KETONE	6	10	5,825
B	TOLUENE DIISOCYANATE	5	39	6,325
B	ETHYLENE TETRACHLORIDE	5	21	5,190
P	SODIUM HYDROSULFITE	5	13	2,025
P	SODIUM CYANIDE	5	11	2,630
B	POTASSIUM HYDROXIDE	4	22	1,740
P	ANHYDROUS ALUMINIUM CHLORIDE	4	5	6,640
B	HYDROGEN PEROXIDE	3	23	9,815
B	TOLUENE	3	23	4,445
B	SULFURIC ACID	3	19	7,325
B	DICHLOROMETHANE	3	16	4,245
B	SODIUM SULFIDE	3	5	1,615
P	THIOGLYCOLIC ACID	3	0	547
P	PHOSPHORIC ANHYDRIDE	3	0	286
B	PHOSPHORIC ACID	2	33	215,900
B	PHENOL	2	12	5,665
B	FORMIC ACID	2	9	1,690
B	TRICHLORETHYLENE	2	8	1,590
B	NITRIC ACID	2	4	1,145
P	ARSENIOUS ANHYDRIDE	1	50	4,660
B	BUTYLACRYLATE	1	25	1,000
B	TETRAETHYLLEAD	1	10	5,980
B	SODIUM NITRITE	1	7	2,345
P	ETHYL GLYCOL	1	6	221
P	ETHYL GLYCOL ACETATE	1	5	318
P	DIMETHOATE	1	4	1,325
B	DIACETONE ALCOHOL	1	4	902
B	DICHLORO - 1,2 ETHANE	1	2	3,735
P	POTASSIUM NITRATE	1	2	127
P	SODIUM CHLORATE	1	0	549
B	TRICHLORETHANE	1	0	545
B	ACETONE	1	0	44
B	XYLENE	0	76	31,790
B	ETHANOL	0	12	13,310
B	NITROMETHANE	0	10	410
B	N and ISOBUTANOL	0	8	16,245
B	ISOPROPANOL	0	8	424
P	BUTYL GLYCOL	0	7	347
B	ETHYL HEXANOL	0	6	26,630
B	TRICHLOROBENZENE	0	6	1,435
B	ETHANOLAMINE	0	6	616
B	HYDROCHLORIC ACID	0	5	3,425
B	CHLORACETIC ACID	0	5	1,805
B	MONOETHYLENE GLYCOL	0	4	6,730
B	MONOPROPYLENE GLYCOL	0	3	4,520
P	DIMETHYLETHYLAMINE	0	3	305
P	SODIUM PENTACHLOROPHENATE	0	3	227
P	METHYL-4 PENTANOL-2 (isobutylmethylcarbinol)	0	3	100
B	FERROSILICON	0	2	17,990
B	CHLOROFORM	0	2	7,150
B	HEPTANOIC ACID	0	2	3,710
P	ARSENIC	0	2	561
P	TRIMETHYLACETYL CHLORIDE	0	2	475
B	OXALIC ACID	0	2	405
P	CHLORACETYL CHLORIDE	0	2	385
P	BUTYL PHENOL	0	2	250
B	MALEIC ANHYDRIDE	0	2	242
B	CHLOROSULFONIC ACID	0	2	212
P	XYLIDINE	0	2	127
P	FORMOL	0	2	58
P	DIMETHYLDICHLOROSILANE	0	2	51
P	METHYLDICHLOROSILANE	0	2	51
B	METHANOL	0	1	6,925
B	METHYL KETONE	0	1	2,785
B	DICHLOROBENZENE	0	1	2,005
P	CALCIUM CARBIDE	0	1	933
B	ACRYLAMIDE	0	1	461
P	TRINITROTOLUENE	0	1	300
B	CALCIUM HYPOCHLORITE	0	1	203
B	MORPHOLINE	0	1	173
P	SODIUM ARSENITE	0	1	137
P	AMMONIUM BIFLUORIDE	0	1	84
B	PROPIONIC ACID	0	1	55
P	CYCLOODECATRIENE	0	1	48
P	ARSENIC PENTOXIDE	0	1	34
B	CYCLOHEXANE	0	1	11
P	ETHYL HEXYL	0	1	11

**Table 9 : RISK OF RELEASE OF CHEMICALS (GN L-GPL, BULK AND PACKED CHEMICALS),  
FOR SHIP ROUTES TO AND FROM MARSEILLE-FOS.**

<u>LIQUEFIED GASES TO AND FROM MARSEILLE/Fos</u> (ALL YEAR 1985) (IGC)		<u>BULK CHEMICALS LOADED AND UNLOADED AT MARSEILLE-FOS</u> ( > 30 MOVEMENTS / YEAR)			
NAME	ONE CASUALTY EACH	NAME	ONE CASUALTY EACH	NAME	ONE CASUALTY EACH
BUTANE	20.7 YEARS	SULFUR	17.4 YEARS	METHANOL	62.7 YEARS
METHANE	27.0 "	SODIUM HYDROXIDE	18.5 "	DICHLOROMETHANE	64.9 "
PROPANE	28.0 "	HYDROGEN PEROXIDE	22.8 "	METHYLISOBUTYLKETONE	67.3 "
BROMOMETHANE	43.3 "	TOLUENE DIISOCYANATE	23.7 "	NITRIC ACID	67.3 "
ETHYLENE	49.3 "	PHOSPHORIC ACID	28.0 "	TETRAETHYLLEAD	82.2 "
VINYLCHLORIDE	285 "	XYLENE	29.6 "	TRICHLOROBENZENE	86.0 "
PROPYLENE	308 "	SULFURIC ACID	31.9 "	TRICHLORETHYLENE	94.9 "
ISOPROPYLAMINE	336 "	FERROSILICON	33.0 "	SODIUM SULFIDE	100 "
ETHYLENE OXIDE	370 "	POTASSIUM HYDROXIDE	35.9 "	BUTYL ACRYLATE	100 "
BUTADIENE	411 "	SODIUM NITRITE	42.5 "	ISOPROPANOL	109 "
		ETHANOL	44.0 "	DIPENTENE	112 "
		BENZENE	46.2 "	N and ISO BUTANOL	123 "
		AMMONIUM NITRATE	46.2 "	DIACETONE ALCOHOL	132 "
		HYDROCHLORIC ACID	47.4 "	CALCIUM HYPOCHLORITE	168 "
		FORMIC ACID	48.7 "	CHLOROFORM	218 "
		ETHYLENE TETRACHLORIDE	52.9 "	VINYLACETATE	217 "
		METHYLETHYL KETONE	56.1 "	PHENOL	231 "
		ACETIC ACID	56.1 "	DICHLOROBENZENE	264 "
		TOLUENE	56.9 "		
		TRICHLORETHANE	56.9 "		

<u>PACKED CHEMICALS LOADED AND UNLOADED AT MARSEILLE-FOS</u> ( > 30 MOVEMENTS / YEAR)			
NAME	ONE CASUALTY EACH	NAME	ONE CASUALTY EACH
DICHLORODIFLUOROMETHANE	11.4 YEARS	THIOGLYCOLIC ACID	142. YEARS
BARYUM CHLORIDE	14.0 "	DIMETHOATE	168 "
CHLORODIFLUOROMETHANE	20.0 "	ANHYDROUS ALUMINIUM CHLORIDE	176 "
HYDRAZINE	30.8 "	HEXAMETHYLENE TETRAMINE	195 "
ARSENIOUS ANHYDRIDE	36.3 "	ETHYLGLYCOL ACETATE	195 "
CARBON DIOXIDE	43.5 "	SODIUM CHLORATE	218 "
CALCIUM CARBIDE	49.3 "	ETHYL GLYCOL	218 "
SODIUM HYDROSULFITE	51.4 "	SODIUM ARSENITE	218 "
TRIMETHYLACETYLCHLORIDE	56.9 "	SODIUM BISULFATE	247 "
SODIUM CYANIDE	64.9 "	SODIUM PENTACHLOROPHENATE	247 "
CALCIUM SILICIDE	67.3 "	CARBON SULFIDE	308 "
OXYGEN	67.3 "	POTASSIUM NITRATE	370 "
THIONYL CHLORIDE	80.4 "		
PHOSPHORUS	82.2 "		
SODIUM CHLORITE	92.5 "		
FORMOL	112 "		
NITROGEN PROTOXIDE	123 "		
SODIUM NITRATE	123 "		



Table 10 = MEAN TONNAGE PER CHEMICAL AND PER MOVEMENT CARRIER  
(a : BULK CHEMICALS, c : LIQUEFIED GASES)

Table 10 a :

LOADED AND UNLOADED CHEMICALS AT MARSEILLE/FOS BULK CHEMICALS	MEAN TONNAGE movement
SODIUM HYDROXIDE	6,370
SULFUR	2,045
DIISOBUTYLENE	1,500
PHOSPHORIC ACID	1,335
BENZENE	1,180
ETHYL HEXANOL	1,160
DICHLORO-1,2 ETHANE	934
HEPTANOIC ACID	928
MONOETHYLENE GLYCOL	897
DIETHYL HEXYL PHTALATE	800
MONOPROPYLENE GLYCOL	695
DIPROPYLENE GLYCOL	518
CHLOROFORM	421
N and ISO-BUTANOL	388
PHENOL	354
METHYL KETONE	348
TRIETHYLAMINE	298
XYLENE	254
DICHLOROPHENOL	181
FERROSILICON	161
ETHANOL	158
DICHLOROBENZENE	143
TETRAETHYLLEAD	139
METHANOL	117
CHLORACETIC ACID	106
AMMONIUM NITRATE	95
METHYLETHYL KETONE	88
METHYLISOBUTYLKETONE	85
DICHLOROMETHANE	75
TETRACHLORETHYLENE	74
ACETIC ACID	71
TOLUENE	68
SULFURIC ACID	63
HYDROGEN PEROXIDE	61
OXALIC ACID	51
VINYL ACETATE	46
HYDROCHLORIC ACID	44
SODIUM SULFIDE	44
CHLOROSULFONIC ACID	42
TOLUENE DIISOCYANATE	41
TRICHLOR ETHYLENE	41
TITANIUM TETRACHLORIDE	39
ACRYLAMIDE	38
TRICHLOROBENZENE	37
PARACRESOL	34
DIACETONE ALCOHOL	32
SODIUM NITRITE	27
BUTYLACRYLATE	27
ETHANOLAMINE	27
NITROMETHANE	24
PROPIONIC ACID	23

(Continue)	MEAN TONNAGE movement
MALEIC ANHYDRIDE	22
PHOSPHORUS TRICHLORIDE	20
FORMIC ACID	19
MORPHOLINE	19
TRIMETHYLAMINE	19
NITRIC ACID	17
DIPENTENE	17
BUTYL METHACRYLATE	17
POTASSIUM HYDROXIDE	17
ACETONE	15
ISOPROPANOL	12
TOLUIDINE	12
CYCLOHEXANE	11
DICYCLOPENTADIENE	11
TRICHLORETHANE	9
CALCIUM HYPOCHLORITE	9
ISOBUTYL ACETATE	9
FERRIC CHLORIDE	6

Table 10 c :

LIQUEFIED * GASES TO AND FROM MARSEILLE/FOS (ALL YEAR 1985) (IGC)	MEAN TONNAGE/ MOVEMENT
METHANE	17,500
PROPANE	2,800
VINYLCHLORIDE	2,400
BUTANE	2,100
BUTADIENE	1,700
DIISOBUTYLENE	1,500
PROPYLENE	1,000
ISOPROPYLAMINE	50
ETHYL ETHER	30
BROMOMETHANE	5
ETHYLENE OXIDE	5

\* Source : IFREMER and MARSEILLES  
PORT AUTHORITY

Table 10 b = MEAN TONNAGE PER PACKED CHEMICAL AND PER MOVEMENT CARRIER

LOADED AND UNLOADED CHEMICALS AT MARSEILLE/FOS PACKED CHEMICALS	MEAN TONNAGE movement	CONTINUE	MEAN TONNAGE movement
ANHYDROUS ALUMINIUM- CHLORIDE	412	METHYL CHLOROFORMATE	16
PHOSPHORUS PEROXIDE	80	BARYUM CHLORIDE	15
DIMETHYLETHER ACETAMIDE	69	PHOSPHORUS	15
SODIUM CYANIDE	66	SODIUM PENTACHLOROPHENATE	15
TRINITROTOLUENE	60	METHYLISOCYANATE	15
ARSENIC	47	PARATHION	15
ARSENIOUS ANHYDRIDE	46	FORMOL	14
CADMIUM	43	METHYL CARBONATE	14
CHROMIUM TRIOXIDE	42	SODIUM CHLORITE	13
DIMETHOATE	38	ETHYL GLYCOL	13
CARBON SULFIDE	38	POTASSIUM NITRATE	13
D.D.T.	36	DIMETHYLDICHLOROSILANE	13
ADIPIC ACID	36	METHYLDICHLOROSILANE	13
CHLORACETYL CHLORIDE	35	CALCIUM CARBIDE	12
DICHLOROPHENYLISOCYANATE	33	AMMONIUM BIFLUORIDE	12
SODIUM CHLORATE	32	DIETHYLDICHLOROSILANE	11
BUTYL PHENOL	31	ETHYL HEXYL	11
XYLIDINE	31	HYDRAZINE	10
SODIUM HYDROSULFITE	28	ZINC PHOSPHIDE	10
LINDANE	25	CALCIUM SILICIDE	9
CYCLODODECATRIENE	24	SODIUM ARSENITE	8
THIOGLYCOLIC ACID	21	ETHYL .2 HEXYLCHLOROFORMATE	8
PARAPHENITIDINE	21	BENZOYL PEROXIDE	8
METHYL GLYCOL	21	DICHLORODIFLUOROMETHANE	7
PARAFORMALDEHYDE	21	TRIMETHYLACETYLCHLORIDE	7
BUTYL GLYCOL	20	SODIUM	7
DIMETHYLETHYLAMINE	20	SODIUM NITRATE	6
SODIUM BISULFATE	19	PARADICHLOROBENZENE	6
PHOSPHORIC ACID	19	HYDROQUINONE	5
HEXAMETHYLENE TETRAMINE	18	CHLORODIFLUOROMETHANE	4
ETHYL GLYCOL ACETATE	18	RESORCINOL	4
NICKEL NITRATE	18	ETHYL ORTHOFORMATE	4
ARSENIC ACID	18	CARBON DIOXIDE	3
METHYL-4 PENTANOL-2	17	THIONYL CHLORIDE	3
ETHYL CHLOROFORMATE	17	PHOSPHORUS PENTASULFIDE	3
ARSENIC PENTOXIDE	17	OXYGEN	2
ISOBUTYL CHLOROFORMATE	17	METALDEHYDE	2
		NITROGEN PROTOXIDE	2

years and for products transported in a packaged form, 1 accident every 1.6 years. Ships transporting Sulfur and sodium hydroxide have the highest risk of accident with 1 every 18 years. Dichlorodifluoromethane and barium chloride have accident probability of once every 11 and 14 years, respectively.

The likelihood of an accident involving H.M. carriers is about 0.6/year\* for LG + bulk + packaged chemicals ; this deals only with vessels calling at the Port of Marseille-Fos.

## **7. HAZARDS FOR MAN AND THE ENVIRONMENT IN THE CASE OF A CHEMICAL SPILL**

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### **7.1 General considerations**

After evaluating the likelihood of accidents and the subsequent likelihood of hazardous chemical (H.M.) release, it is important to assess the hazards posed to man and the environment which will vary according to the nature and the volume of spills.

Main hazardous factors are flammability and risk of explosion. (Two other factors are the toxicity and corrosion). The flammability factor relates to most part of the derivatives of the petrochemical industry (classified as 2.1, 3.1, 4.1 in the IMDG Code). The flammable substances cover a large group of products - gases, liquids or solids - often present in the bulk or packed tankers' cargos.

A particular place must be given to bulk liquefied gases. The hazards due to flammable gases (2.1) are greater than liquids in the same category (3.1) since they are rapidly vaporized in the case of spillage. A fire which occurs near a LPG reservoir causing

\* Calculated on the basis of 6000 ship movements per year of which 3000 are for bulk chemical transportation, 2300 are for chemicals transported in packages and 700 for liquified gases.

the reservoir tank to overhead can lead to a B.L.E.V.E. (Boiling Liquid Expanding Vapor Explosion). Flammable liquids can form explosive mixtures with air, especially if they are confined.

Flammable solids (classes 4.1 and 4.2) such as white phosphorus or calcium carbide are able to burn due to spontaneous combustion or by reacting with water in order to release flammable gases.

In addition to hazards related to the flammability (fire, explosion, burns) those due to a chemical's toxicity can be two fold :

- intoxication or asphyxia due to toxic vapors
- skin damages

This is observed when the substances give rise to a toxic gas cloud which may extend over a much larger distance than the chemical spill itself.

All these aspects are described in the "IMO Antipollution Manual on Spillages other than Oil" whose first section evaluates the dangers related to chemical spills.

Among the methods used to quantify dangers for man and the environment :

- classification of chemicals according to their physical properties (density, vapor pressure, miscibility with water) : evaporators, floaters, dissolvers, sinkers. (See Table 12 for the name group explanation).
- a classification of chemicals according to their toxicity for man and the environment (see annex IV)

7.2. Classifications applied to chemicals transported by vessels calling at the Port of Marseilles-Fos.

In order to evaluate the dangers related to H.M. transportation in the Mediterranean, and those related to loading or unloading at Marseilles-Fos, three tables have been prepared :

- i) a calculation of transported tonnage for each chemical, per movement (Tables 10 a-b-c)
- ii) a classification of chemicals (in decreasing tonnages), dangerous for the environment ( Z or + in Column A, 3 or 4 in Column B, or XX or XXX in Column E) and for man (II in Column D) (Tables 11, a, b, c, d) and annex IV for the GESAMP categories.
- iii) For substances most often transported (in tonnage) chemicals from Categories I, IIb and IIIb (presenting dangers to man) and from III and IV (dangers for the environment), the risk of release was evaluated (table 12)

Table 10a gives the average tonnage loaded on a ship for each bulk chemical : sodium hydroxide is the product whose unit tonnage is the highest (more than 6000 tons). For organic chemicals, diisobutylene, benzene and ethyl hexanol are loaded at more than 1000 tons per carrier.

Table 10b gives the same information for chemicals transported in a packaged form. The individual tonnages do not exceed 100 tons except for anhydrous aluminum chloride whose cargo weight per ship is about 400 tons.

The chemicals which are hazardous to man or to the environment are shown in Table 11.

For LPG (Table 10c), propane, butane and vinyl chloride have the most tonnage per ship (between 2000 and 3000 tons)

Benzene is among the products which are the most hazardous to the environment and the most often transported in bulk, at about 100 000 tons per year. Several other hazardous substances are transported at tonnages less than 10 000 tons/year such as chloroform, toluene, diisocyanate, tetraethyl lead and phenol (Table 11a).

Among packaged chemicals considered most dangerous for the environment, (table 11b) arsenious anhydride is more often transported in the Mediterranean (about 5,000 tons/year) than even in other seas. Other hazardous substances, which are listed in a decreasing order according to for their tonnages, are sodium cyanide, sodium hydrosulfite, dimethoate, and hydrazine.

Paradoxically, we have not listed methyl parathion for more than 10 tons per cargo because this organic phosphorus is transported in large quantities (approximately 1500 tons/year) for the French ports of the Atlantic (CEDRE report R 86.216 R).

The following products are toxic for man and are the most often transported :

- among the products transported in Bulk (Table 11c), 17 substances have been listed of which 9 are carried with tonnages greater than 1000 tons per year : benzene, toluene diisocyanate, tetra ethyl lead, phenol, dichloro-1, 2 ethane, sodium sulfide, trichloroethylene, dichlorophenol, nitric acid.

- among the packaged products (Table 11d), 3 substances are transported with an annual weight greater than 1,000 tons per year hydrazine with 1,255 tons, sodium hydrosulfite with 2,024 tons, arsenious anhydride with 4,875 tons (which is equal to about 20,000 drums of 250 kilograms per year).

The hazards for man and the environment of the principal chemical groups are shown in Table 12. According to the RIJKSWATERSTAAT groups I, II b and III b are the most hazardous to man while the chemicals of groups III and IV are the most noxious for the environment.

Table 11 :

11 a - BULK CHEMICALS INVOLVING THE HIGHEST RISK  
FOR THE ENVIRONMENT.

LOADED AND UNLOADED CHEMICALS AT MARSEILLES/FOS <u>BULK CHEMICALS</u>	ANNUAL TONNAGE
BENZENE	94,400
CHLOROFORM	7,150
TOLUENE DIISOCYANATE	6,325
TETRA ETHYLLEAD	5,980
PHENOL	5,665
ETHYLENE TETRACHLORIDE	5,190
DICHLORO-1,2 ETHANE	3,735
SODIUM NITRITE	2,345
DICHLOROBENZENE	2,005
SODIUM SULFIDE	1,615
TRICHLORETHYLENE	1,590
TRICHLOROBENZENE	1,435
DICHLOROPHENOL	1,355
ALKYLBENZENE	1,000
TRICHLORETHANE	545
ACRYLAMIDE	461
ISOPROPANOL	424
TITANIUM TETRACHLORIDE	351
MALEIC ANHYDRIDE	242
CALCIUM HYPOCHLORIDE	203
PHOSPHORUS TRICHLORIDE	183
TOLUIDINE	47
PARACRESOL	34

Table 11 :

11 b - PACKED CHEMICALS INVOLVING THE HIGHEST RISK  
FOR THE ENVIRONMENT.

LOADED AND UNLOADED CHEMICALS AT MARSEILLES/FOS <u>PACKED CHEMICALS</u>	ANNUAL TONNAGE
ARSENIOUS ANHYDRIDE	4,460
SODIUM CYANIDE	2,630
SODIUM HYDROSULFITE	2,025
DIMETHOATE	1,325
HYDRAZINE	1,255
PHOSPHORUS	690
ARSENIC	561
THIOGLYCOLIC ACID	547
CARBON SULFIDE	447
TRINITROTOLUENE	300
CARBON DIOXIDE	240
SODIUM PENTACHLOROPHENATE	227
D.D.T.	182
LINDANE	178
SODIUM ARSENITE	137
METHYL CARBONATE	98
CHROMIUM TRIOXIDE	85
METHYLCHLOROFORMATE	80
PHOSPHORUS PEROXIDE	80
ZINC PHOSPHIDE	50
ETHYLCHLOROFORMATE	50
CYCLODODECATRIENE	48
CADMIUM	43
ARSENIC PENTOXIDE	34
ARSENIC ACID	18
PARATHION	15



Table 11 :

11 c - BULK CHEMICALS INVOLVING THE HIGHEST RISK  
FOR MAN.

LOADED AND UNLOADED CHEMICALS AT MARSEILLES/FOS <u>BULK CHEMICALS</u>	ANNUAL TONNAGE
BENZENE	94,400
TOLUENE DIISOCYANATE	6,325
TETRAETHYLLEAD	5,980
PHENOL	5,665
DICHLORO-1,2 ETHANE	3,725
SODIUM SULFIDE	1,615
TRICHLORETHYLENE	1,590
DICHLOROPHENOL	1,355
NITRIC ACID	1,145
ACRYLAMIDE	0461
ISOPROPANOL	0424
TITANIUM TETRACHLORIDE	0351
MALEIC ANHYDRIDE	0242
PHOSPHORUS TRICHLORIDE	0183
TOLUIDINE	0047
PARACRESOL	0034
CYCLOHEXANE	0011

Table 11 :

11 d - PACKED CHEMICALS INVOLVING THE HIGHEST RISK  
FOR MAN.

LOADED AND UNLOADED CHEMICALS AT MARSEILLES/FOS <u>PACKED CHEMICALS</u>	ANNUAL TONNAGE
ARSENIOUS ANHYDRIDE	4,875
SODIUM HYDROSULFITE	2,024
HYDRAZINE	1,255
PHOSPHORUS	0690
ARSENIC	0561
THIOGLYCOLIC ACID	0547
PARAPHENITIDINE	0368
TRINITROTOLUENE	0300
CARBON DIOXIDE	0240
THIONYLCHLORIDE	0143
XYLIDINE	0127
METHYL CARBONATE	0098
DICHLOROPHENYLISOCYANATE	0082
METHYL CHLOROFORMATE	0080
PHOSPHORUS PEROXIDE	0080
METHYL DICHLOROSILANE	0051
DIMETHYL DICHLOROSILANE	0051
ZINC PHOSPHIDE	0050
ETHYL CHLOROFORMATE	0050
CYCLODODECATRIENE	0048
CADMIUM	0043
METHYL ISOCYANATE	0015
PARATHION	0015
DIETHYL DICHLOROSILANE	0011

Table 12 : RISK OF RELEASE BASED UPON CHEMICAL GROUPS FOR THE 39 MOST TRANSPORTED BULK CHEMICALS (90% IN YEARLY MOVEMENTS) AND RESPECTIVE THREATS FOR MAN AND ENVIRONMENT.

CHEMICAL GROUP	ANNUAL MOVEMENTS	ONE CASUALTY EACH :	HAZARD : - M FOR MAN - E FOR ENVIRONMENT
I	33	112 YEARS	M
II a	8	460 "	/
II b	372	10 "	M
TOTAL II	380	10 "	M
III a	989	4 "	E
III b	118	31 "	M
III c	378	10 "	E
TOTAL III	1485	3 "	M, E
IV a	622	6 "	E
IV c	156	24 "	E
TOTAL IV	778	5 "	E

IDENTIFICATION OF THE CHEMICAL GROUPS CITED IN THE TABLE 12

GROUP I : EVAPORATORS

Chemicals carried pressurized or undercooled.

I-A: lighter density relative to air.  
rapid dispersion.

I-B: heavier density relative to air.  
specific cautions must be applied.

GROUP II: FLOATERS

Group IIa.

Floating substances slowly evaporating, but not dissolving.

Group IIb.

Floating substances and evaporating. Depending on the vapour pressure explosive and/or toxic gas concentrations may be produced above the floating pollutant.

Group IIc.

Floating substances, slowly dissolving or reacting with water.

GROUP III: DISSOLVERS/MIXERS

Group IIIa.

Substances dissolving in water, not reacting with water and not rapidly evaporating

Group IIIb.

Substances dissolving in water, rapidly gasifying or evaporating.

In spite of dissolving, inflammable mixtures may form above the watersurface.

Group IIIc.

Substances reacting with water and dissolving.

GROUP IV: SINKERS

Group IVa.

Sinking substances not soluble and not reacting with water

Group IVb.

Substances initially sinking, than refloating

Group IVc.

Substances initially sinking. Afterwards dissolving or reacting with water

The probability of an accident associated with each chemical group has also been determined for the chemicals themselves (table 9). The chemicals of group III (about 1 casualty every 3 years) and more specifically group III-a (1 casualty every 4 years) have the highest rate of risk.

### **7.3. Environmental Vulnerability Index**

A method for measuring the coastline's vulnerability to oil spills, which could be considered an environmental sensitivity index, has been perfected by CEDRE to predict the effect of an oil spill on a coastline's fishing and aquacultural resources. This method which was originally designed with oil spills is also able to be applied to some large scale floating chemical spills. The index will permit estimations of the quantity (in tons) of shellfish and fish which will be damaged on a given coastline in the event of a spill. The method takes into consideration the depth and the geomorphology of the coast.

This information can be found in an Atlas which also lists - using well explained maps - all the necessary information for pollution control operations in order to preserve the maritime patrimony. The data have been published in the CEDRE Report "Atlas of the Rhone Delta and its Surroundings".

## **8. CONCLUSIONS ON THE RISK ASSESSMENT OF MARINE CASUALTIES INVOLVING HAZARDOUS SUBSTANCES CARRIED BY SHIPS IN THE MEDITERRANEAN**

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The major point deals with the large amount of traffic of hazardous substances occurring in the Mediterranean and especially for carriers crossing via the Suez Canal or the Bosphorus and Gibraltar, and those loading or unloading at the Spanish, French or Italian petrochemical complexes. An increasing accident risk is the result of the increased chemical transport especially near the straits (Gibraltar, Bosphorus, Messina), the trade routes along certain coastal areas (Cabo-da-Gata in Spain, along the Italian peninsula, in the Greek archipelago), or in zones of traffic

intersection or convergence. Although the casualties qualified as "serious" have only rarely involved carriers of liquefied gases or chemicals, the likelihood of a chemical spill related to such accidents will increase with an increase in our needs for natural resources and energy. An obvious example is an increase in maritime transportation of gasoline boosters which are based on ether or methanol, and which will progressively replace lead derivatives in anti-knock gasoline.

Generally, very few products are transported in bulk and in large quantity (more than 100,000 tons/year) but there are numerous chemicals which are shipped in small quantities and the products which have the greatest tonnage (sodium hydroxide, sulfur, phosphoric acid) are not the most dangerous.

For the packed chemicals (43 % of ships' movements, 2.4 % of total tonnage), the cargos do not exceed 10,000 tons per year, and the most often transported cargos are less than 100 tons (per chemical and per movement) and are generally hazardous for man or the environment. Containers of dangerous substances are able to be swept overboard, especially when carried on the deck. If the containers are not recovered they can deteriorate and cause damage.

The hydrological particularities of the Mediterranean, the diversity of biological species, make this area vulnerable. The large amount of hazardous substances' maritime traffic (a great many products with a small tonnage) leads to a need to preserve the Mediterranean, especially along the coastlines where the major part of the traffic takes place, from any chemical spillage.

**Table 14 : REQUIRED SORBENT RATIO FOR SORPTION OF CHEMICALS**

CHEMICAL NAMES	CHEMICAL WEIGHT (g)	DRY "BULTHANE" WEIGHT (g)	OPTIMUM RATIOS (in weight)
Butanol	24,1	1,2	r = 20
Butyl Acetate	23,8	0,9	r = 26
Cumène	24,1	1,8	r = 13
Cyclohexane	24,7	1,1	r = 22
Cyclohexanone	24,0	0,8	r = 30
Méthyl-éthyl-kétone	24,3	1,3	r = 19
Méthyl-isobutyl-kétone	24,0	1,3	r = 18
Toluène	24,7	1,5	r = 16
Xylène	24,0	1,4	r = 17

**in "Absorption et Agglomération de produits chimiques"  
CEDRE Report n° R.86.193.R., 1986, by H. DIDIER**

Table 15. Minimum Amount of Gelling Agents Required to Form an Immobile Gel (g/10 ml)

MINIMUM AMOUNT OF GELLING AGENTS REQUIRED TO FORM AN IMMOBILE GEL (g/10 ml)					
Chemical (10 ml)	"M" Gelgard (grams)	Imbiber Beads (grams)	1422 Hycar (2% Cabosil) (grams)	Carbopol (grams)	Blend A* (grams)
Acetone	----	----	0.58	1.38	1.15
Acetone Cyanohydrin	11.6	----	1.23	2.64	2.10
Acrylonitrile	5.47	4.21	0.58	1.43	1.25
Ammonium Hydroxide	0.22	----	----	----	0.32
Aniline	----	----	0.72	----	1.47
Benzaldehyde	----	2.95	0.54	----	1.57
Benzene	----	0.58	0.54	----	0.59
Butanol	----	----	----	0.74	1.74
Carbon Disulfide	7.56	0.79	2.50	----	1.25
Carbon Tetrachloride	----	0.42	----	1.41	1.20
Chlorine Water	0.14	----	----	----	0.47
Chloroform	----	0.47	0.33	----	0.76
Cyclohexane	----	0.95	----	----	0.88
Cyclohexanone	----	2.52	0.54	----	1.35
Ethanol	----	----	----	0.52	0.98
Ethyl Acetate	----	0.89	0.72	----	1.05
Ethylene Dichloride	----	1.10	0.43	----	1.05
Ethylene Glycol	4.32	----	----	0.67	0.78
Formaldehyde	0.58	----	----	0.74	0.52
Gasoline	----	0.74	3.62	----	1.27
Isoprene	----	0.42	1.52	----	0.83
Isopropyl Alcohol	----	----	----	1.11	1.94
Kerosene	----	2.37	6.11	----	1.94
Methanol	----	----	----	0.57	1.03
Methylethyl Ketone	----	0.84	0.54	----	1.13
Octane	----	4.05	----	1.61	1.89
o-Dichlorobenzene	----	0.74	0.51	----	1.08
Petroleum Ether	3.74	0.58	2.17	----	1.03
Phenol	----	----	0.54	1.80	1.20
Pyridine	----	1.58	0.51	----	1.03
Sulfuric Acid	1.22	----	1.45	----	0.98
Tetrahydrofuran	----	0.68	0.47	0.94	0.76
Trichloroethylene	----	0.63	0.47	----	0.81
Water	0.07	----	----	----	0.12
Xylene	----	0.74	1.09	----	1.18

\* 20% of each of following ingredients: Gelgard, Imbiber Beads, Hycar (2% Cabosil), Carbopol and Cabosil.

## OPTIMIZATION OF UNIVERSAL GELLING AGENT AND DEVELOPMENT OF MEANS OF APPLYING TO SPILLED HAZARDOUS MATERIALS

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Application of Annex II of the 73/78 MARPOL convention and the eventual installation of a Mediterranean VTS will considerably lower the risks. However, in the meantime, and probably during the next 10 years, as we observe an augmentation in chemical transportation (increased "finished chemicals" production in the Middle East, increased consumption in southern Europe) risks of serious casualties involving H.M. will increase. In the event of a spill, it will be necessary to intervene with a maximum of speed and efficiency in order to minimize the hazards for man, as well as for the environment and even for the ships themselves.

#### 9 - DESCRIPTION OF THE PROBLEMS ASSOCIATED WITH COMBATING MARINE POLLUTION BY HAZARDOUS SUBSTANCES - AN OVERVIEW -

Numerous information which deal with a control of marine pollution by hazardous substances - and some specific problems - have been presented in 1986 during the course : "HAZARDOUS MATERIAL SPILL IN THE MARITIME SECTOR" organized at the Rotterdam International Safety Centre (R.I.S.C.), on behalf of the Commission of the European Communities. Studies presented by D. Cormack, W. Koops, B. Loostrom, H.J.G. Walenkamp and J.A.C. Van Rooy described case studies of accidents, what needs to be done for hazardous chemical spills and what is the best response to specific hazardous chemical(s) behaviour. (cf. annex IX)

In the event of an accidental marine pollution involving hazardous cargoes, it is most important to know the exact nature and tonnage of involved chemicals, and also the oceanographic feature and topography of the bottom (in the case of sinkers) at the accident's location.

Computer models, like HACS, or response manuals (like the Tanker Safety Guide, the CHRIS manual, the UK Department Trade's SEACHEM, the CANUTEC manuals) are useful to predict the chemicals' behaviour, to assess the risk and to give informations for an appropriate intervention.

Also, specific countermeasures have to be undertaken in view of combating spillages, especially for floaters, dissolvers/dispersers or sinkers. The case of volatile chemicals is a special one because of the potentially toxic cloud formation and dangers of flamability.

### 9.1- Available data

The United States has already worked in this field for many years ; in 1972, there was a program developing "first generation" technology for hazardous materials spill control. The Coast Guard and Environmental Protection Agency (E.P.A.) are involved in the control of accidental spills respectively on sea and on land.

For this reason, the Coast Guard designed the CHRIS (Chemical Hazard Response Information System) on the basis of bibliographic data. This manual file gives the physical characteristics, the toxicity for aquatic life, the hazards for water intakes and the countermeasures when available, for 1,000 substances. Furthermore, a hazard assessment computer system will determine for a lake or a river the arrival time, concentration and duration of a pollution, the countermeasure, and the amount of products needed.

In the EPA laboratory, experiments are carried out to determine the aquatic toxicity of some substances and to improve the countermeasures available. They use the NIH/EPA Chemical Information System in which data banks such as the following are stored :

- OHM-TADS (Oil and Hazardous Materials - Technical Assistance Data System) : data concerning 1000 substances transported in large quantities,
- RTECS (Registry of Toxic Effects of Chemical Substances) made by the National Institute of Occupational Safety and Health ; it contains 40 000 toxicity measures, some concerning aquatic life.

The Manufacturing Chemists Association, designed CHEMTREC (Chemical Transportation Emergency Center), is a round-the-clock emergency service, which can give information on hazards of many chemical products and rapidly alert the chemical company official when an accident occurs.

When the Coast Guard are asked information on a product which is not listed in their file, they refer you to CHEMTREC.

- U.K. is now finishing a file on 100 to 200 products carried in bulk, giving their toxicity and the countermeasures to use when a spill occurs at sea. The London fire brigade has the use of a HAZCHEM micro-card system for 6000 products.

- Germany has a data bank (DABAWAS) for 3500 products containing their physical and toxicological data (mainly aquatic), their ability to damage the environment and the countermeasures to use when an accident occurs.

- The EEC has launched a project ECDIN which would stock data on 25 000 products. This project is now in its first stage and freely available, but does not have much data. Even if the main priority is based on the collection of physical, chemical and toxicological data for a small amount of products, the operational stage will not be available before 4 to 5 years.

- IRPTC (International Register on Potentially Toxic Chemicals), of UNEP and IPCS (International Program on Chemical Safety), of WHO, both in Geneva, have relevant information for the most toxic substances indispensable for H.M. behaviour knowledge in case of an intervention.

- In France, some data are stored in different banks (INSERM, IRCHA) and in chemical companies. On the other hand, the French fire brigade has set up a list of all dangerous products carried in France (whatever their means of transportation) which allows an immediate identification of the substance involved in an

accident. For each of these 8000 products the card will contain physical, chemical and toxicological characteristics, the hazards and the countermeasures.

- Other countries such as Sweden, the Netherlands and Belgium have developed structures to deal with accidental spills.

### 9.2. Check-up of countermeasures

The first thing to do in case of an H.M. spillage is to look at the lightening possibility in view of minimizing the release at sea of hazardous substances. It is in this framework that CEDRE, in 1986, looked at the possibilities of use of on-board equipment or additional equipment for off loading the hazardous cargo of a disabled ship (R.86.210.C). Indeed, each tank is generally equipped with a hydraulic submerge pump. Tankers are also, in many cases, equipped with a hydraulic central powerpack.

From the point of view of discharging in water, three characteristics are of prime interest. The first is the specific gravity of the substance, i.e. whether it will sink or float ; the second is the miscibility of the substance, i.e. whether it will mix, dissolve or remain a cohesive whole which can be tracked and attacked, the third one is the vapour pressure.

Products which float and do not mix in water are the easiest to deal with, since methods have been developed to combat oil spills for many years.

The others are considerably more difficult to handle ; nevertheless, some experiments and researches concern :

- booms
- dredging for sinking products
- stirring to improve dispersion
- sorbents, dispersants, neutralizing products...

It is useful to consider counter pollution methods for each category :

- a) for gas clouds (extracted from "Response Measures for Chemical Spillage, BAWG-OTSOPA 10/12/1-E by D. Cormack)

Evaporation of volatile components from crude oil spills removes all those with boiling points  $< 250^{\circ}\text{C}$  in a few hours. Such evaporation does not appear to give rise to hazardous atmospheres outside the confines of the slick but within the slick itself, when fresh, there is the possibility of fire where the volatile components of the surface slick burn leaving a heavy residue. Much effort has been devoted in the past to the intentional combustion of oil slicks as a means of removal but without success. It is found that the thinness of the surface layer, the water temperature beneath, and the presence of non-volatile components will prevent complete combustion. With pure chemicals of suitable volatility, however, this might be a feasible solution in certain cases.

High volatility on the other hand gives rise to concern regarding the possibility of toxic or explosive vapour clouds even at a distance from the spill. There is much talk of the possible need to evacuate local populations. Decisions on this will obviously be dependent on the ability to predict concentrations of a product in the atmosphere at a distance from the spill. Assessment must obviously be done on a predictive basis as evacuation, if required, must clearly be carried out prior to the arrival of the cloud. Analytical detection methods will be of more use in subsequently declaring the evacuated area safe again.

Similar considerations apply to traffic at sea in the vicinity of the slick and it may be necessary to close areas down wind of the casualty. Again at sea and from the point of view of beach use, where soluble products are involved, there will be concern to know on a predictive basis, the concentration of a product in the sea.

At least, we have to inform that CEDRE, in cooperation with

CEPPOL, defined and tested a chemical protected cloth for intervention in polluted areas.

b) for floaters

The intervention, by chemical or mechanical means, is dependent on the ability of the chemicals to dissolve/evaporate, i.e. to persist at the surface of the water.

- treating of floating spills of chemicals by sorbents  
(extracted from "treating of floating spills of chemicals on the water surface by systems using sorbent materials or other agents", Swedish Board of Customs, Coasts Guard H.Q., by B. Looström)

Spills into the water of liquid chemicals, with density less than water and which are insoluble or very slightly soluble in water, behave in a similar way to oil spills. Such chemical spills can, in principle, be recovered in the same way as oil spills. Mineral oils are generally rather viscous and form more or less thick layers on the water surface which are very often available for recovery actions. This distinguishes oils from many chemicals.

Most of the liquid chemicals, which are carried at sea, are less viscous than mineral oils. When spilled into the water, such chemicals rapidly form thin layers on the water surface which are most difficult to recover than most oils. Nevertheless it has been shown that recovery of certain floating chemicals can be performed and will be enhanced by using sorbents and other treating agents.

During experiments in a large (20 x 200 metres) U.S. Environmental Protection Agency test tank (OHMSETT), spilled octanol and dioctylphthalate have been successfully recovered by a system using small polyurethane sorbent cubes as well as a system with an oleophilic rope. At the exhibition of the 1986 Hazardous Material Spills Conference, St Louis, Missouri, information was given about recovery of a xylene spill by means of 3M sorbent (polypropylene) and an oleophilic rope (oil Mop). Other sorbents are based on a t-butyl styrene polymer (DOW Chemical).

Laboratory experiments done at CEDRE (1986), showed that :

- adapted sorbents can be used to soak up most floating and insoluble hazardous chemicals
- a subsequent packing is not strong enough to enable its collection by trawling at high speed.

Table 15 shows the required chemical/sorbent ratio.

- use of gelling agents (extracted from Looström, same reference as above and from the EPA Project summary "Three new techniques for floating pollutant spill control and recovery", by Bannister et al.)

Several experiments and trials have been performed with agents that thicken spilled chemicals to gels and thus make them easier to handle. The purpose is to increase the thickness of the layers of spilled chemicals on the water surface and thus facilitate recovery by means of skimmers or similar equipment.

An E.P.A. paper deals with recovery of floating hazardous materials spills in water bodies by amine carbamate gelling agents and with two methods for locating near surface pollutants : fluorescent agents for nighttime operations and "environmental sonic sensing".

Amine carbamate gelling agents can be used to gel oil and floating HM spills quickly and completely to a solid consistency. This gel is much more visible than the liquid pollutant, does not readily flow or spread, is very easily, quickly, and completely recovered by nets or sieves, is much less volatile (and thus less hazardous with regard to fire and toxicity), does not permeate sand or other porous materials, and can be easily regenerated into the original pollutant and gelling components.

Efforts to optimise the use of gelling agents have been done by Michalovic et al who prepared table n° 15. They concluded that the experiments produced good results ; however a parameter which must also be considered is the elevated price of the gelling agents.

However, gelling agents - as well as sorbents - are limited to spillages of small extent.

- dispersing HM spills (Extracted from "Response to Oil and Chemical Marine Pollution, by Cormack, 1983, and from a DORNIER/FSSH paper intitled "Transport von Chemikalien auf See", 1983).

The viscosities of bulk chemical cargoes suggest that they will, in the majority of cases, be amenable to dispersant treatment. Indeed, by analogy to the case of light diesel oil it could be considered that natural dispersion will be so rapid that the application of dispersants is unnecessary. However, in some cases the hazards to human health may be such that it would be unacceptable, if at all avoidable, to have a particular chemical come ashore. This is true for the substances for which counter-measures are only possible on a short term basis : aniline ; N-butanol ; Adiponitrile. These substances evaporate relatively quickly and present particular health, fire and explosion hazards, and it would be preferable to disperse them. Objections to such a course of action are difficult to sustain irregardless of any damage to the marine environment. According to Cormack (1983), the use of aircraft spraying means that the dispersant can be applied to the chemical from a relatively safe position for the anti-pollution personnel compared to that of ship-board application.

- Mechanical recovery of floating spilled chemicals (from Cormack, 1983, same reference as above).

If chemicals are solid at ambient temperatures, nets, screens or creepers can be used.

Booms and skimmers may be used for chemical spills in some cases. However, hazardous materials which could be physically recoverable may not in fact be safe to handle in this way. With hazardous material of this type the best approach will be to disperse.



A recent CEDRE report (R.86.225.C) deals with containment and recovery of pollutants discharged from chemical carriers. It concerns the adaptation of existing equipment, such as FRAMO TK 5, TK 6, TK 8, MARFLEX pumps and recovery devices such as "SIRENE" and "POLLUTANK" which can be used for the recovery of various hazardous chemicals. Laboratory experiments were also performed to estimate the aggressive behaviour of chemicals on equipment components like pump bodies, tubes, joints, ...

c) for dissolvers (Extracted from "Hazard assessment and identification of dissolvers and dispersers", by B. Looström, R.I.S.C., 1986 and the paper presented at BAWG-OTSOPA/12/12/4-E by Germany. on hazard potential and combatting possibilities of H.M.

Some types of treating agents for use in actions against spills of mixers are :

- neutralizing agents (against acids and bases : sodium bicarbonate and sodium dihydrogen phosphate, respectively).
- activated carbon
- flocculating agents
- oxidizing agents
- reducing agents
- complexing agents
- ion exchangers

These methods, however, have a disadvantage in that neutralizing additives are to be used. With the flocculation method, miscible chemicals are to be sunk, with subsequent removal by dredging. This method, however, has the great disadvantage of spreading the flocculated chemical cloud, owing to the low sinking speed of the flocculents and the drifting occurring during this process.

Therefore, the recovery efficiency will not be very high. If the water/chemical cloud is removed by pumping and fed into an adsorber facility the chemicals could be generally reprocessed. Studies have shown, however, that - apart from transport problems - the recovery and disposal of chemical additives (such as activated coal) and the detection of the water/chemical cloud involved major difficulties.

d) for sinking substances (extracted from BAWG-OTSOPA 12/12/4 - E - n° 12 - same reference than above)-

In the case of sinking substances the problem of ecological pollution has been shifted to the bottom, but the danger has not been eliminated in principle. The main problem with sinking substances is the question of rediscovering their position. Owing to currents and rough sea, the substances, depending on their density, will drift away in a vane, individual portions will disaggregate and spread further, so that the ideal case of a stationary pool must be considered an exception. It is necessary to develop special measuring procedures in order to determine the precise location of the chemical. In this connection, it would be possible to carry out measurements of the water body with analogously working measuring techniques, such as the acquisition of the pH value or of the conductivity of the substances. According to this continuously working method, a limited sea area would have to be scanned in a chequerboard manner to detect the location of a liquid pool. A search of the area by sampling and wet-chemical analysis technique at any rate would be slower and more time-consuming than the above-mentioned analogous search and thus would be too complicated for an efficient planning of the recovery operation. If the substance can be located at the sea bottom, it could be removed from the sea bottom by suction dredging. For this purpose the operation would have to be carried out without the water jets provided for stirring up the bottom.

The proportion of removed parts of silt, sand and chemicals is difficult to predict, but in the case of an assumed layer of the chemical with a thickness of only 10 cm the contents should mainly be water, sand and silt. The removed substance/water mixture could be pre-separated in the cargo hold by gravity separation, with the excessive water being drained off immediately into the sea via overflow orifices.

Dredging will presumably be contemplated only if a nonsoluble material is involved. Even low-solubility materials will eventually dissolve and be removed by dilution in the sea. The recovery of soluble pollutants by processing contaminated sea water will presumably not become a routine spillage response operation.

Suction dredgers can operate at the sea bottom down to a water depth of approximately 30 m. In deeper waters other methods, for example the air lift technique developed for the exploration of nodular manganese, would have to be applied. In estuaries the intake capacity may be considerably reduced owing to uneven bottom conditions.

e) for packaged goods D. Cormack's opinion, extracted from "present state of development in hazardous material spillage response" (RISC) is the following :

Intact packages, if floating, may of course be a hazard to navigation and should be treated accordingly. If sunk they may be trawled up in nets. Again with intact packages this should present no more hazard than any other operation in the normal handling of intact packages which incidentally are designed for safe handling. Decisions about Search and Recovery in the short term can therefore be taken calmly.

Only those packages which after a long period of exposure on the sea bed may leak and damage the environment or those in a leaking which state pose a threat to fishermen need be candidates for search and recovery. Other products may also be sought and

recovered but here it is appropriate to keep in mind other factors such as dilution rates in the environment and a reduced threat even if fishermen do recover a leaking package. Finally, in very many cases, there is no need at all to search and recover packages on the sea bed.

When packages do come ashore it is important to recognise that the task is not to instruct the general public in how to handle them. The only instruction the public needs is to leave the packages alone. Existing organisations and available expertise can handle, recover and dispose of any packages which do come ashore.

For illustration, we have included, in appendix VIII, a now 7 years old document, written by Bjorn Looström, which gives an overview on hazard evaluation and response for 4 selected chemicals (ammonia, benzene, acrylonitrile and creosote).

A project carried out by IFREMER, in collaboration with CEDRE and the Company "AEROSPATIALE", intends to assess the risk of pollution due to H.M. shipping in a packaged form. Around 500 chemicals (IMDG classes 1 to 9) have been collected from the Marseilles Port Authority's data. For each chemical, the following informations are available : name, formula, identification of the chemical, date, route, ship's characteristics (type, G.R.T., draught, docks, packs localisation), chemical weight, number of movements, nature of the packing (inside, outside). Data collection will be concluded on march 1987 and the risk assessment study by the end of 1987.

### 9.3. Need to integrate chemical spill response into national existing contingency plans.

Contingency plans have, up to now, concentrated on oil spill response. (ITOPF, 1983, ROCC 1986, see bibliography) Due to the threat of the increasing traffic of chemicals in the Mediterranean, especially in terms of number of movements and of the diversity of the products, it is necessary to include some

specific responses dealing with hazardous substances other than oil in existing national contingency plans.

The Mediterranean Sea presents hydrological and biological characteristics which makes it an area more vulnerable than the open ocean.

Cooperation with the various Mediterranean countries in the area of preventing H.M. spills or combating an eventual accident would be most useful in safeguarding human lives and preserving the marine environment in case of serious casualties.

To give an idea of what sort of recommendations can be proposed, we have reproduced, as an example, the chapter n° 5 of the BAWG-OTSOPA-15/14/2-E (Apr. 1986). Report intituled "Present work on matters concerning chemical spill response within the Bonn Agreement and in particular within the Netherlands".

1. The on-duty officers, on-scene commanders must be trained to be "specialists" in controlling and combating spillages of hazardous substances other than oil. Special attention should be paid to situation analysis and decision analysis.

2. Striketeam crews and others involved should be trained in measuring techniques, safety aspects, and hazards.

3. Hazard identification and response/decision systems implemented on a fully manned, round the clock, computer should be set up to assist the on-duty officer, on-scene commanders and decision-making team in effective and quick response.

4. Off-shore teams specialised in countermeasures should be made available in case of marine casualty (e.g. fire-brigades, chemical industry etc.).

5. In all cases where decision analysis and executing the plan can be postponed for a few days "outdoor specialists" must be consulted.

6. Emergency procedures and response routines should be set up where a distinction can be made in immediate response and normal response.

7. Decision and action procedures should be clearly laid down to facilitate rapid response to an emergency.

## 10 - PROPOSAL OF A PROGRAM TO BE CARRIED OUT BY THE ROCC

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One of the points of the overview to be carried out by CEDRE in the IMO request concerns recommendations for specific actions to be conducted, through the ROCC, in collaboration with Mediterranean countries.

In light of preceding presentation, some proposals can be made :

- making contact with regional officers of the COST-301 program
- writing a new chapter - dealing with chemicals - in the ROCC guide for combating pollution in the Mediterranean
- proposing training courses which are both general and specialized
- organizing a workshop on maritime traffic of hazardous substances in the Mediterranean and the need to integrate chemical spill response into existing national contingency plans.
- placing a chemist, specialized in aspects of combating hazardous chemicals, on the ROCC staff.

a) Contacts with the regional officers of the COST-301 program

The "Istituto per l'Automazione de la Navigazione", in Genoa, which collects all the traffic data for the whole Mediterranean, will be able to furnish data dealing with maritime traffic or casualties in a "few weeks" delay.

It will be therefore useful to first look into the possibility of access to the data (listings, soft-ware transfer) within the framework of an eventual cooperation between ROCC and COST-301 related organisms.

- b) Writing a new chapter, concerning hazardous chemicals, in the ROCC guide for combating pollution in the Mediterranean.

The ROCC's guide intitled "guide for oil pollution combating in the Mediterranean" could be adapted to chemical spill control by adding a new chapter, with special attention to the most threatened geographic areas and the most critical chemicals.

- c) Organization of general or specialized training courses

- "general" training courses : That concerns the necessity to

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introduce, in the existing training courses, aspects dealing with the chemicals' behaviour and their control in case of spillage. Among the points which could be considered :

- a knowledge of the potential hazards when shipping dangerous goods.
- the prevention of pollution by a respect for reglementation, especially concerning the bulk and packed chemicals.

It is from this point of view that the next MEDIPOL (April 6-16, 1987) has provided in its programme a presentation of some aspects dealing with hazardous chemicals control.

- "specialized" training courses in hazardous chemicals control in

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case of spillage :

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This training course should be oriented towards an optimization of the various Mediterranean countries' intervention capacities ; the related points could be :

- Knowledge of procedure for the anti-pollution personnel in case



of emergency (specialized clothing, aircraft, etc.).

- Understanding which cases of chemical spills can and should be controlled, and how.
- Information circulation between Mediterranean countries in case of serious casualties.
- Optimization of an installation of intervention means.

This type of specialized training course, concerning more specific aspects, demands an important organization with an implementation of equipment and means of intervention.

d) Organization of a workshop, on a Mediterranean level, which would have for objective to exchange and to gain information on :

- . maritime traffic of dangerous goods in the Mediterranean
- . contingency plans content in order to include elements related to intervention and combating chemicals in case of spillage.

Topics of such a workshop could concern :

- a compilation of all information contained in the existing guides on combating pollution as well as in computerized systems (i.e. HACCS), allowing the prediction of actions immediately after the accident for the information of the anti-pollution personnel.
- a study of "model accidents", followed by adapted proposals for an intervention. These studies would be based on real or "potential" cases and would allow adapted responses in function of :
  - . physico-chemical and toxicological behaviour of the specific chemical,
  - . meteo-oceanographic conditions.

e) Addition of a chemist in the ROCC staff

To facilitate the implementation of such a programme, it is necessary to take advantage of transfers or changes in the ROCC staff in order to include a good level Chemical Expert.

DATA SOURCES \*

Data from IMO, Lloyd's, BAWG, UNEP, COST 301, MARIN, DMI, FSSH, SCG, USCG, Rijkswaterstaat, RISC, French Navy (CECMED/PREMAR III), CROSSMED, IFP, IFREMER, DPNM, MAVRAC, Marseilles Harbour Authority, GAZOCEAN, SHOM, CEPPOL CEDRE, and Canadian, Greek, Italian and U.K reports have been used for this study

\* See last page "Glossary of abbreviations".

**ANNEXES**

**ANNEX I**



Existing methods for studying

Reliability or security

(in : Bureau Veritas, 1985 : Study of the possibility  
of doing a risk assessment analysis for pollution of  
the french Coastline).

## PROBABILITY SKETCH

Drawing an adapted probability sketch, integrating all the parameters listed above, relies on the following method :

### - Analysis of the pollution processes :

It concerns the establishment of all the scenarios which could lead to pollution. This study covers all the known hazardous substances, the types of carriers and the various types of packaging.

### - Laws of probability

An establishment of the laws of a probability of pollution relies on the preceding analysis and demands a quantification of the influence of certain parameters.

Once the laws of probability have been determined, the probability of pollution for a given vessel, product, packaging or environment can be defined.

## Utilization

Such a level of precision in assessing a risk gives rise to an understanding of the probabilities of pollution :

- . by coastline
- . by product
- . by the type of carrier
- . by the quantity transported

or any combination of these diverse variables.

The probability of pollution occurrence being known, an estimation of the seriousness of the pollution enables a calculation for the "parameter of criticality".

$$C_i = P_i \times \lambda_i$$

When :

- $C_i$  = criticality
- $\lambda_i$  = probability of occurrence
- $P_i$  = a parameter for the seriousness of the consequences

Once the parameter of criticalness has been obtained, the hierarchy for risk levels associated with each product can be determined.

The results of a probability analysis have a direct implication on a definition of the means of intervention :

- Optimizing a geographic installation of intervention material.
- Optimizing the capacities of intervention in relation to the transported tonnages
- Optimizing the means of intervention in relation to the products (material, protection, training programs...).
- Preparation of a manual of intervention procedures adapted to the most critical products.

### Methods

The methods available for dealing with studies of reliability or of security are two sorts :

- . inductive methods
- . failure trees

## 1 - INDUCTIVE METHODS

### 1.1 - FMEA (Failure Mode and Effect Analysis).

This type of method is generally used for :

- analysing the consequences of failure which could affect material or a system.
- identifying the breakdowns having serious consequences according to different criteria such as :

The success of missions related to the systems, the availability, the costs of maintenance, security...

If the FMEA method is only interested in the criterion of security, the research objectives are :

- to identify the modes of breakdown and errors which could be detrimental to good working order and to determine the cause,
- to establish, from among the breakdowns and errors, the list of those having the most serious consequences on the security,
- to determine, for each breakdown or error, the detection procedures and the repairs to be put into action,
- to insure that the probability of each breakdown and error has been sufficiently reduced,
- to insure that the influence of each breakdown or error on the security has been sufficiently reduced,



At this level it is possible to introduce the quantitative parameter of "criticality" in order to evaluate the pair probability - seriousness. (The parameter of criticality  $C_i$  is the product of an hourly probability represented by  $\lambda_i$  multiplied by a factor  $P_i$  which quantifies the seriousness of the consequences).

- to provide the persons who are responsible for technical choices with qualitative and quantitative elements which are relative to the security.

## 1.2 - PRELIMINARY RISK ANALYSIS

The method is intended :

- to identify
  - . dangerous elements
  - . dangerous situations
  - . potential accidents
- to determine the seriousness of the consequences and to define the procedures enabling a mastery of dangerous situations, and to eliminate potential accidents.

Preliminary risk analyses are presented in the form of tables of columns which are read from left to right according to the principal which consists to imagine how, for a given under-system in a given phase of functioning, a dangerous situation could be transformed into an accident and what are the consequences of the accident.

The columns correspond to the following ideas :

1. Sub-system or function : an identification of the total system
2. Phase : identification of the modes of utilization during which certain aspects of the whole could give rise to a risk,

3. dangerous elements : identification of those elements which can be associated with an intrinsic danger,
4. event causing a dangerous situation : identification of the conditions, undesirable events, breakdowns or errors which could transform a dangerous element into a dangerous situation,
5. Dangerous situation : identification of dangerous situations which are the result of an interaction between a dangerous element and the entire system following an event described in 4,
6. Event causing a potential accident : identification of the conditions undesirable events, breakdowns or errors which can transform a dangerous situation into an accident,
7. Potential accident : identification of accident possibilities which are the result of dangerous situations following an event described in 6,
8. Consequences : identification of the consequences of potential accidents,
9. Classification by seriousness : a qualitative measure of the seriousness of the consequences. For example, according to the MIL. STD 882 norm : Minor, significant, critical, catastrophic,
10. Preventive measures : a compilation of proposed measures for eliminating or controlling the identified risks,
11. Application of the preventive measures : a collection of information dealing with :
  - . The effectiveness of the preventive measures
  - . Their introduction into the utilization procedures or into the system itself.

## 2 - FAILURE TREE

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### 2.1 - Description of the method

The method known of the "failure tree" is a deductive method which moves from a well defined undesirable event in order to graphically reconstitute combinations of events which could lead to the undesirable out come.

A failure tree is made up of successive levels so that each event is generated by events in the next lowest level on the basis of logical out comes. The deductive process is followed back until we arrive at the base or root events which are characterized by the following criteria :

- They are independent from each other,
- Their probabilities can be estimated,
- Specialists do not require their being broken down into simpler events.

These elementary events can be of any nature such as :  
Break downs, human errors, atmospheric conditions,  
earthquakes...

An analysis by the failure tree method can be made in six steps :

- 1) Definition of the undesirable event
- 2) Examination of the system
- 3) Construction of the failure tree
- 4) Collection of quantitative data
- 5) Probability evaluation
- 6) Analysis of the results.

### **- Definition of the Indesirable Event**

In principle this step is very simple.

In fact, it is necessary to analyse the system sufficiently before making a choice. An undesirable event which is too general will give a failure tree which is so complicated that it will be impossible to deal with it.

### **- Examination of the System**

It is indispensable to have an excellent knowledge of the entire system and the utilization procedures. These imperatives require a pluri-disciplinary team where each member has a thorough knowledge of his subject.

### **Construction of a failure tree.**

The failure tree is made up of successive levels which are related to each other by logical premises (mainly the ideas are connected by "AND", "OR" and "IF" which give a good understanding and precise formalization).

### **Quantitative Data Collection.**

It is necessary to make up a catalogue where the random variables which are characteristic for the probability of each elementary event are defined.

Whether or not the tree is related to time, the quantitative data will permit an estimation for the frequency of probability or a understanding of the time-dependent functions for certain random variables.

### **Evaluation of the Probability**

This step requires a global determination for the probability of an undesirable event but also defines the most critical passages and calculates the probability for all of them.

When a tree is not time-dependent, the final probability is calculated using the Algebraic rules of Boole. When a tree is time-dependent, methods of simulation enable a calculation of the probabilities for the most critical passages.

In each case, when the number of drawings necessary for determining the critical passages becomes prohibitive, we can fall back on the methods used for reducing variance which can considerably reduce computer time while maintaining a method with an acceptable precision.

#### - Analysis of Results.

An analysis of the failure tree enables :

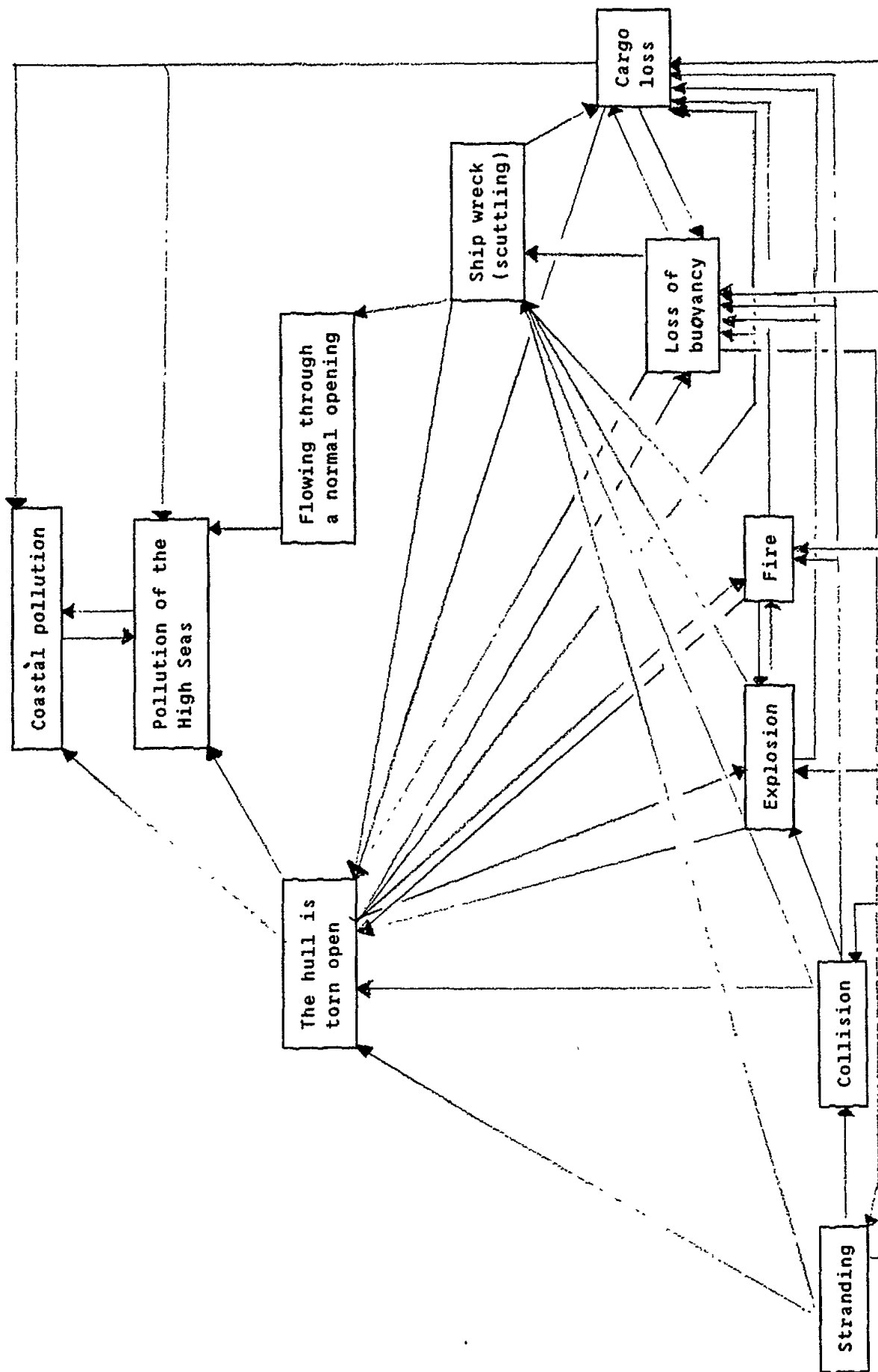
- a calculation for the probability of an undesirable event,
- a determination of the critical passages,
- an elimination of incorrect redundancies which give the illusion of security.

The underlining of a given event's influence which can occur in several critical developments.

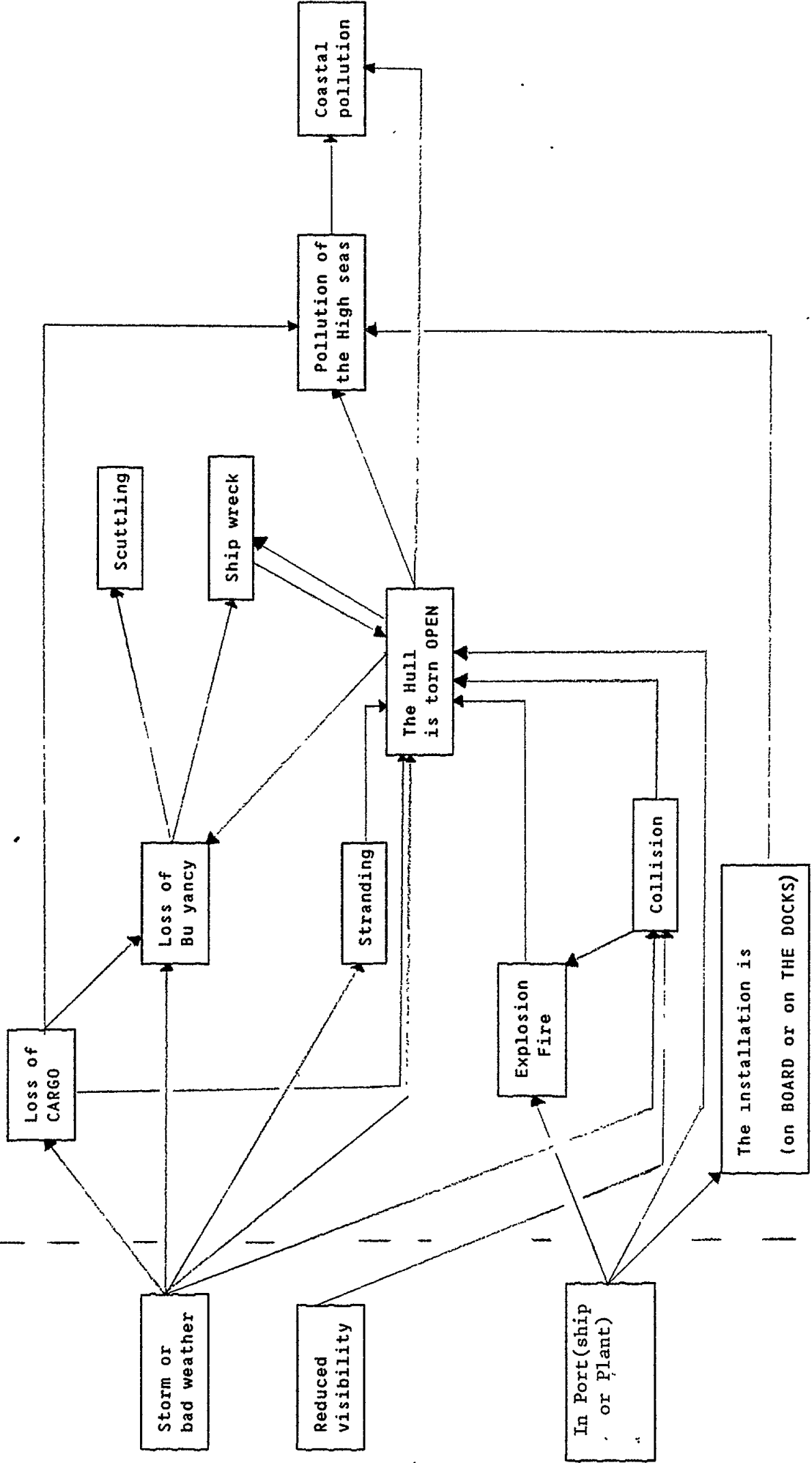
**ANNEX II**



Graphs summarizing the accident scenarios  
and the preliminary risk assessment,  
obtained from data of accidents  
along the French coastline  
(CEDRE Report, 1982)



GRAPH OF PRELIMINARY RISK ASSESSMENT



GRAPH SUMMARIZING ACCIDENT SCENARIOS



**ANNEX III**



**LIST OF BASE EVENTS**

(This list has been made in order to assess the risks of an oil spillage, but can be extended to floating H.M. spillages).

ELEMENTS NATURELS (1 à 53)

- 1 Visibilité réduite (brouillard,.....)
- 2 Mauvaise visibilité au coucher ou au lever du jour
- 3 Vent (responsable d'une forte mer)
- 4 Vent vers la côte (entraînant un navire)
- 5 Vent vers la côte (entraînant une nappe d'hydrocarbure, au point 1)
- 6 Vent dirigé vers la mer (entraînant une nappe d'hydrocarbure à partir d'un point différent de 1)
- 7 Vent insuffisant pour permettre une évaporation totale
- 8 Vent suffisant pour permettre un début d'évaporation
- 9 Soleil insuffisant pour permettre une évaporation totale
- 10 Soleil suffisant pour permettre un début d'évaporation
- 11 Météo empêchant d'effectuer un allègement (état de la mer pour le navire, Météo... pour l'hélicoptère)
- 12 La météo a empêché d'alléger dès le début (mais a évolué favorablement après)
- 13 La météo s'est dégradée au point de nécessiter l'interruption de l'allègement
- 14 Météo empêchant une intervention de remorqueur
- 15 La météo a empêché de déclencher l'opération de remorquage dès le début (mais a évolué favorablement)
- 16 La météo s'est dégradée faisant échouer le remorquage
- 17 La météo empêche l'opération de colmatage ou de pompage
- 18 Courants (responsables d'une forte mer)
- 19 Courants vers la côte (entraînant un navire)
- 20 Courants vers la côte (entraînant une nappe d'hydrocarbure du point 1)
- 21 Courants dirigés vers la mer (entraînant une nappe d'hydrocarbure à partir d'un point différent de 1)
- 22 Les courants au fond sont trop importants pour effectuer un pompage sur l'épave
- 23 Les courants sont trop importants pour effectuer un colmatage (celui-ci ayant lieu au fond ou à la surface)

- 24 Courants dont la composante perpendiculaire au barrage est supérieure à 1 noeud
- 25 Courants de surface insuffisants pour permettre l'étalement de la nappe
- 26 La cargaison est projetée sur le navire (du fait de l'état de la mer)
- 27 Mer agitée : creux supérieure à 1.5 m (empêchant la pose de barrage ou la récupération d'hydrocarbures)
- 28 Mer agitée empêchant tout traitement (force 5 et plus)
- 29 Brassage du produit effectué rapidement (présence de houle)
- 30 Houle (favorisant la dérive du navire vers la côte)
- 31 Absence de marée à l'endroit de l'échouement
- 32 Présence de marée à l'endroit de l'échouement
- 33 Mer haute lors de l'échouement
- 34 Zone où la marée est importante (le navire, même bien posé, se déchirera du seul fait de la pression due à sa cargaison non compensée par celle de l'eau)
- 35 Côtes de rochers
- 36 Plage de sable
- 37 Plage de galets
- 38 Les remorqueurs ne peuvent pas accéder au lieu d'intervention (topographie...)
- 39 Présence d'obstacles résistants autour du lieu d'échouement (ils vont entraver les manoeuvres de dégagements)
- 40 Présence d'obstacles autour du navire (le bloquent et l'empêchent de se dégager)
- 41 Présence d'obstacles tels que le navire échoué est bloqué et déchiré (le remorquage est impossible)
- 42 Obstacle en mer (banc de sable, récif,....)
- 43 Obstacle souple (vase,....)
- 44 Fonds marins meubles
- 45 Configurations des fonds défavorables (le navire se retrouve en porte-à-faux)
- 46 Site de déversement inaccessible pour un alléger (pas assez de place....)

- 47 L'épave est inaccessible pour un pompage (profondeur)
- 48 Topographie (responsable d'une forte mer : profondeur des fonds, forme .....)
- 49 Tranche d'eau importante (sur le lieu de l'échouement)
- 50 Zone ne pouvant pas être protégée par des barrages (trop étendue,.....)
- 51 Zone sensible (emploi d'agent coulant proscrit)
- 52 Zone sensible (emploi de dispersant proscrit)
- 53 Pas d'agent coulant naturel en quantité suffisante (plancton,.....)

MATERIEL (54 à 84)

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- 54 Rupture du matériel de chargement ou déchargement (tuyaux, vannes.... entre le navire et l'installation de réception.)
- 55 Rupture d'un collecteur de circuit d'hydrocarbure près d'une source de chaleur
- 56 Le navire embarque de l'eau par un collecteur défaillant (rupture d'un collecteur de prise d'eau)
- 57 Le navire embarque de l'eau par un panneau de cale (cas des Vraquiers)
- 58 Gite ou assiette trop importante dans la tempête (due à une perte de chargement....)
- 59 Perte de chargement due à une rupture d'un des matériels d'arrimage (cable...)
- 60 Echauffement excessif d'un moteur (pompe par exemple) lors des opérations de chargement ou déchargement
- 61 Echauffement excessif d'un moteur en mer (moteurs différents de ceux utilisés lors des opérations de chargement)
- 62 Frottement anormal produisant un échauffement (au niveau d'arbre de transmission, paliers....)
- 63 Feu dans les circuits électriques
- 64 Chute d'une pièce métallique contre les parois de la citerne (outil, boulon) au port
- 65 Chute d'une pièce métallique contre les parois de la citerne (outil, boulon) en mer
- 66 Avarie de barre
- 67 Avarie de propulsion

- 68 Perte de manoeuvrabilité à proximité d'un navire (avarie propulsion barre)
- 69 Vétusté du navire (d'où coque fragile)
- 70 Corrosion externe anormale (d'où coque fragile)
- 71 Présence de rouille sur les parois de la citerne
- 72 Radar en panne
- 73 Moyen de contrôle du chargement (sonde....) défaillant
- 74 Non fonctionnement du matériel de mouillage
- 75 Non fonctionnement du matériel de détection d'hydrocarbure (IR....)
- 76 Non fonctionnement du matériel de transmission radio
- 77 Le matériel d'allègement s'est avéré inadéquate
- 78 Le matériel de remorquage s'est avéré inadéquate
- 79 Panne du matériel embarqué pour l'allègement (pompe...)
- 80 Panne du matériel de remorquage
- 81 Avarie du remorqueur
- 82 Avarie du navire allègueur
- 83 Pas de protection de la citerne (absence de compartiment vide)
- 84 Pas de radar

#### CARGAISON (85 à 105)

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- 85 Présence de vapeurs de carburants dans la citerne (absence d'oxygène du fait d'un système d'inertage)
- 86 Présence de vapeurs inflammables dans la citerne (carburant + oxygène)
- 87 Présence de vapeurs inflammables au-dessus du navire en mer (due à différentes opérations : entretien, dégazage....)
- 88 Une quantité importante d'hydrocarbure était présente
- 89 Quantité trop importante de produit déversé pour permettre une évaporation totale des fractions évaporables
- 90 Le pétrole contient du soufre
- 91 Produit peu sensible aux agents coulants (produits lourds)
- 92 Le produit contient une quantité de produits tensioactifs insuffisante
- 93 Le produit contient une quantité importante d'asphaltènes et de résines

- 94 Le produit ne se prête pas à un allègement ou à un pompage (il est trop visqueux)
- 95 Le produit est trop visqueux pour être récolté par pompage en mer
- 96 Le produit est trop visqueux pour être dispersé
- 97 Le produit n'est pas assez visqueux pour être récolté par chalutage
- 98 Le produit n'est pas constitué seulement de fractions légères
- 99 Le produit n'est composé que de fractions légères
- 100 Présence de fractions non évaporables ou non solubles de densité inférieure à 1
- 101 Toutes les fractions de densité inférieure à 1 sont évaporables ou solubles
- 102 Densité initiale du produit inférieure à 1
- 103 La cargaison flotte au moins momentanément (cargaison autre qu'hydrocarbures)
- 104 La cargaison flotte (cargaison autre qu'hydrocarbures)
- 105 Auto-inflammation de la cargaison (fermentation de coton, ballast....)

#### LES OPERATIONS OU SITUATIONS DE NAVIGATION NORMALES (106 à 117)

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- 106 Introduction d'oxygène (lors d'une intervention dans une citerne,....)
- 107 Citerne sous gaz inerte
- 108 Projection d'eau (lors du lavage des citernes) créant de l'électricité statique
- 109 Projection de crude (lors du lavage des citernes) créant de l'électricité statique
- 110 Projection de pétrole (lors du remplissage des citernes) créant de l'électricité statique
- 111 Opération de déchargement
- 112 Ballastage (rejette les vapeurs inflammables au-dessus du navire)
- 113 Travail avec une source de chaleur (chalumeau,...) lors d'opérations d'entretien de routine
- 114 Les navires sont contrebordiers (font la même route en sens inverse)

- 115 Les routes des navires se croisent (mais ont des directions différentes)  
 116 Un des navires rattrape l'autre  
 117 L'atterrissage (l'approche de la terre)

ELEMENTS HUMAINS (118 à 182)  
 -----

- 118 Déversement accidentel au port dû à une erreur humaine lors des opérations de chargement ou déchargement (erreur d'ouverture d'une vanne ....)  
 119 Perte de chargement due à un mauvais arrimage (cas d'un porte conteneurs ....)  
 120 Perte de chargement par largage volontaire (pour rééquilibrer le navire...)  
 121 Mauvaises répartitions de chargement répétées causant une fragilité de la coque  
 122 Erreur humaine entraînant une mauvaise répartition du chargement  
 123 Erreur de manoeuvre à proximité d'un navire  
 124 Rien n'est fait pour éviter la collision car il y a une mauvaise interprétation de la route ou de la vitesse du navire  
 125 La manoeuvre est trop tardive car il y a eu hésitation de la part d'un commandant  
 126 Mauvaise interprétation de la manoeuvre de l'autre navire d'où manoeuvres contradictoires  
 127 Manoeuvre de correction inefficace pour contrer la dérive  
 128 Absence de manoeuvre de correction pour contrer la dérive  
 129 Manoeuvre d'évitement d'un navire gênant (amène à s'approcher dangereusement des côtes)  
 130 Une manoeuvre a permis de partiellement ralentir la dérive  
 131 Chocs répétés d'accostage (erreur de manoeuvre) fragilisant la coque  
 132 Echouage (action volontaire d'échouer un navire)  
 133 Erreur de navigation fatale (se diriger directement vers la côte....)  
 134 Pas de manoeuvre correctrice (pour contrer une manoeuvre initiale dangereuse)  
 135 Non respect de la réglementation (séparation du trafic....)  
 136 Non respect de la réglementation de circulation près des côtes par méconnaissance (grand nombre de règlements parfois différents d'un pays à l'autre)

- 137 Non respect de la réglementation de circulation près des côtes du fait de la difficulté d'application (règlement pas très réaliste)
- 138 Non respect de la réglementation de circulation près des côtes par non respect délibéré (souvent cause économique)
- 139 Erreur de navigation par négligence (ne prend pas ses repères,....)
- 140 Erreur de navigation par mauvaise interprétation due à une modification des moyens de repérage (ces repères ont été détruits, déplacés....)
- 141 Erreur de navigation par mauvaise interprétation due à l'utilisation des cartes périmées
- 142 Erreur de navigation par mauvaise utilisation des données (se tromper de signification....)
- 143 Erreur de navigation par mauvaise condition physique (maladie, alcool....)
- 144 Hésitation à communiquer l'information (de la part du commandant responsable.....)
- 145 Mauvaise connaissance des procédures d'alertes (d'où cheminement trop long avant d'informer les autorités compétentes)
- 146 Le remorquage n'est pas demandé par le navire
- 147 le remorquage n'est pas demandé par le Préfet Maritime
- 148 Pas de veille sur un des navires
- 149 Radar non utilisé (pas de surveillance par radar)
- 150 Apport d'électricité statique venant de l'extérieur de la citerne (fil de nylon, vêtements,....)
- 151 Apport de chaleur divers : cigarette, outillage (aussi bien sur le navire que sur le quai)
- 152 Erreur humaine d'appréciation ou d'interprétation lors de la détection d'une nappe
- 153 Mauvaise évaluation de la dérive des nappes (les modèles ne prennent pas en compte un paramètre important localement...)
- 154 Mauvaise coordination dans l'emploi de plusieurs méthodes (par exemple emploi de dispersant puis tentative de récupérer le produit en mer)
- 155 Mise en oeuvre trop lente des moyens de lutte contre la pollution en mer
- 156 Mauvaise coordination des moyens d'allègement
- 157 Personnel inexpérimenté pour pratiquer un allègement
- 158 Pas d'équipe d'intervention disponible (pour être déposée sur le navire lors du remorquage)
- 159 Déclenchement de l'alerte trop long



- 160 Mauvaise coordination lors du remorquage (entre remorqueur, navire et terre)
- 161 Personnel inexpérimenté pour réaliser un remorquage
- 162 Mauvaise coordination lors de la pose du barrage
- 163 Méthode d'emploi d'agents coulants inadéquate
- 164 Mauvaise utilisation des dispersants (équipage non expérimenté, mauvais choix de produit....)
- 165 Mauvaise coordination des moyens mis en oeuvre pour la récupération par pompage
- 166 Mauvaise coordination des moyens mis en oeuvre pour la récupération par chalutage
- 167 Mauvaise coordination des moyens mis en oeuvre pour l'épandage des dispersants (guidage par avion...)
- 168 Fragilité de la coque due à la construction (conception, réalisation....)
- 169 Mauvaise procédure de lavage des citernes (fragilisation de la coque par corrosion interne)
- 170 L'opération a tardé à être déclenchée à cause d'une mauvaise coordination (recherche de matériel)
- 171 L'opération a tardé à être déclenchée à cause d'un manque d'information (sur la qualité du produit, sur le lieu de déversement)
- 172 Sous évaluation du danger de la part du capitaine (lorsque le navire est en avarie)
- 173 Pas de demande d'assistance (le capitaine ne la juge pas utile)
- 174 Refus de la proposition d'assistance, son coût étant jugé trop élevé
- 175 L'opération de pompage est jugée trop coûteuse (par rapport à une autre méthode, y compris celle de ramasser le pétrole sur la côte)
- 176 L'allègement est jugé trop coûteux (par rapport à une autre méthode, y compris celle de ramasser le pétrole sur la côte)
- 177 L'opération de colmatage est jugée trop coûteuse (par rapport à une autre méthode, y compris celle de ramasser le pétrole sur la côte)
- 178 Plus personne à bord pour effectuer le mouillage (le navire est abandonné)
- 179 Pétardage des citernes intactes (décision prise pour traiter toute la pollution en une seule fois)
- 180 Sabordage du navire
- 181 Acte de piraterie, sabotage, guerre...
- 182 Recherche d'eau calme lors d'une tempête

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 EVENEMENTS NON DECOMPOSES (183 à 253)  
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- 183 Demande d'assistance non captée
- 184 Pas de moyen ayant fonctionné pour repérer le navire en perdition  
(un autre navire sur zone, moyen de surveillance du rail....)
- 185 Pas de surveillance sur zone pour détecter la nappe (navire, avion...)
- 186 Pas de remorqueur disponible à proximité (ceux qui existent sont trop éloignés)
- 187 Pas de remorqueur disponible car ceux qui existent effectuent d'autres interventions
- 188 Le remorqueur met trop de temps à arriver sur les lieux (avarie en cours de trajet...)
- 189 Pas d'alléger disponible (il n'y a pas de navire disponible apte à être transformé en alléger)
- 190 L'alléger n'est pas disponible assez rapidement (délais pour trouver le navire ou pour l'équiper)
- 191 Pas de moyen pour déposer le matériel sur le navire accidenté (hélicoptère venant déposer le groupe de pompage...)
- 192 Les moyens pour déposer le matériel sur le navire accidenté n'ont pas été disponibles assez rapidement
- 193 L'opération de pompage nécessite une technologie longue à mettre en oeuvre
- 194 L'opération de colmatage nécessite une technologie longue à mettre en oeuvre
- 195 Equipe pour le pompage sur l'épave non disponible
- 196 Equipe pour le colmatage non disponible
- 197 Matériel de pompage sur épave non disponible
- 198 Matériel de colmatage non disponible
- 199 Pas de barrage disponible
- 200 Moyen de mise en place des barrages non disponibles
- 201 Agent coulant non disponible
- 202 Moyen d'épandage des agents coulants ou absorbants flottants non disponible
- 203 Pas de produit absorbant flottant disponible

- 204 Navires pour la récupération par pompage non disponibles
- 205 Navires pour la récupération par chalutage non disponibles
- 206 Matériel de récupération par pompage non disponible
- 207 Matériel de stockage pour la méthode de pompage non disponible
- 208 Matériel de chalutage non disponible
- 209 Matériel de stockage pour la méthode de chalutage non disponible
- 210 Dispersant non disponible
- 211 Matériel d'épandage de dispersant non disponible
- 212 Navires pour l'épandage de dispersant non disponibles
- 213 Rupture d'une installation côtière non portuaire
- 214 Rupture d'une installation dans les terres près d'un cours d'eau (cf fiche 39)
- 215 Rupture d'une installation portuaire par collision d'un navire (sea line ....)
- 216 Rupture d'un stockage dans un port
- 217 Rupture d'un pipe dans un port (autre cause qu'une collision de navire)
- 218 Déchirure de la coque sur le fond ou sur un obstacle immergé (présence d'un obstacle surélevé, hauteur d'eau (marée) non prise en compte)
- 219 Déchirure de la coque due à une collision avec une installation
- 220 Déchirure de la coque due à une collision avec un autre navire
- 221 Le déversement à partir d'une installation côtière, n'a pas pu être stoppé rapidement
- 222 Déversement provenant d'une plate-forme
- 223 Le déversement à partir d'une plate-forme pétrolière n'a pas pu être stoppé rapidement
- 224 Le déversement a été très rapide
- 225 Le pétrole arrive trop rapidement à la côte pour permettre une évaporation totale (courant, localisation du déversement....)
- 226 Ecoulement du produit du fait d'une défaillance à bord du navire échoué
- 227 Relargage de la cargaison solide à partir d'une épave au fond
- 228 Collision avec un navire non contrôlé (type KAVO KAMBANOS cf fiche n°7)
- 229 Collision avec une mine

- 230 Collision avec une plate-forme
- 231 Collision avec un bateau feu, bouée ou autre objet immobile....
- 232 Le navire a été repris et emmené en mer (par la mer ou par les hommes)
- 233 Le navire n'a pas coulé avant
- 234 Le navire ne s'est pas échoué définitivement avant
- 235 Navire ayant rompu ses amarres (cas du JUAN A LAVELLAJA cf fiche n°8)
- 236 L'échouement se fait avec une vitesse d'arrivée réduite
- 237 La partie A n'a pas supporté le choc lors de l'échouement
- 238 Déchirure provoquée par un échouement en mer
- 239 Choc violent au fond lors du naufrage
- 240 Choc violent au fond après le naufrage (collision d'un autre navire sur l'épave)
- 241 Citerne de soutes touchée
- 242 Présence d'un compartiment vide (citerne de ballast, peak avant, chambre des pompes....) entre la coque et la citerne de cargaison qu'il protège
- 243 Parois citerne compartiment touchée
- 244 Citerne concernée pleine (soit protégée par un compartiment vide, soit directement contre la coque)
- 245 Pas de réparation de l'avarie (avarie trop grave, équipage non compétent pour cette tâche, équipe d'intervention non disponible....)
- 246 Intervention de remorqueurs
- 247 Taille et état de chargement important (c'est un seuil variable au delà duquel, compte tenu de la vitesse de dérive, le matériel de mouillage ne peut pas résister à la force d'inertie)
- 248 Importance du chargement (suivant l'état du chargement, le navire ne réagira pas de la même façon aux influences des autres facteurs)
- 249 Taille du navire (suivant l'état du chargement, le navire ne réagira pas de la même façon aux influences des autres facteurs)
- 250 Feu dans les emménagements
- 251 Perte de flottabilité
- 252 Brèche trop grande pour permettre un colmatage

253 Feu dans les installations sur le quai ou sur le navire

COMPLEMENTS  
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254 Foudre

255 Tempête

256 Absence de dissolution ou de mise en émulsion quantitative

ANNEX IV

RELATION BETWEEN THE CONDITIONS OF  
THE MARITIME TRANSPORT OF DANGEROUS  
GOODS AND THE PROTECTION OF THE  
MARINE ENVIRONMENT

- FINAL REPORT -  
September 1985

Contract N° : 84-B-6621-11-003-11-N

FORSCHUNGSSTELLE FÜR DIE SEESCHIFFAHRT ZU HAMBURG E.V.  
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The term "harmful substances" is defined in numerous international conventions. All definitions list the objects to be protected from an environment pollution. Subsequently, "harmful Substance" means any substance which, if led into the sea, is liable

- to create hazards to human health,
- to harm living resources and marine life,
- to damage amenities or
- to interfere with other legitimate uses of the sea

(MARPOL Art. II , Interventions Protocol Art. I , London Convention Art. I, Oslo Convention Art. I)

Helsinki (Art II ) extends the objects to be protected to the impairment of the quality for use of sea water and emphasizes that the legitimate use of the sea includes fishing (see also Art. 1 Law of the Sea Convention, 1982).

The Intervention Convention confines the right of intervention to those cases that make it necessary to prevent, mitigate or eliminate grave and imminent danger to the coastline or related interests from pollution following upon a maritime casualty which may reasonably be expected to result in major harmful consequences (Art. I ). "Related interests" also mean the interests of a coastal state directly affected or threatened by a maritime casualty, such as

- maritime, coastal, port, or estuarian activities, including fishery activities constituting an essential means of livelihood for the persons concerned;
- tourist attractions of the area concerned;
- the health of the coastal population and the well-being of the area concerned, including the conservation of living marine resources and wild life.

## CHEMICALS CARRIED IN BULK

According to MARPOL Annex II Reg. 1 "noxious liquid substances" means any substance designated in Appendix II (List of Noxious Liquid Substances Carried in Bulk). Appendix III contains a "List of Other Liquid Substances Carried in Bulk". The substances listed there have been evaluated and found to lie outside the scope of MARPOL Annex II, because they are presently considered as presenting no harm to the marine environment as prescribed by MARPOL (Reg. 4 of Annex II).

Where it is proposed to carry liquid substances in bulk which are enumerated in none of the substance lists, the government of a contracting state involved in the proposed operation shall establish and agree on a provisional assessment of the proposed operation. This proposional assessment shall be based on guidelines for use in the categorization of noxious liquid substances which are given in Appendix I of Annex II (Reg. 3 of Annex II).

Annex II divides the noxious liquid substances into 4 categories depending on their hazard to marine resources, human health, amenities and other legitimate uses of the sea (Reg. 3 of Annex II):

- Category A Substances which justify the application of stringent anti-pollution measures;
- Category B Substances which justify the application of special anti-pollution measures;
- Category C Substances which require special operational conditions;
- Category D Substances which require some attention to operational conditions.



The Guidelines for the Categorization of Noxious Liquid Substances contain a general description of the substances' danger potential (Appendix I of Annex II).

The categorization of substances has been performed by a working group of GESAMP

In order to be able to evaluate the dangers to the marine environment arising when a substance is led into the sea, the GESAMP working group developed a Hazard Evaluation Procedure. According to this procedure the hazard profile of a substance is investigated by means of 5 valuation criteria. These 5 criteria are labelled with the first 5 capital letters of the alphabet and they mean, in abridged form :

- A Bioaccumulation and tainting;
- B Damage to living resources;
- C Hazard to human health, oral intake;
- D Hazard to human health, skin contact and inhalation;
- E Reduction of amenities.

The particular hazards are subdivided into up to 7 danger grades. One danger grade each per criterium is assigned to every substance. This results in a Hazard Profile of the substance.

The transfer of the categorization according to the Hazard Profile Procedure onto MARPOL categories A, B, C and D is effected by means of the classification matrix in Tab. XXXI

Hazard Profile				MARPOL 73 Annex II Pollution Category
A	B	C	E	
*	-	-	-	Category A
-	4	-	-	
T	3	-	-	
Z	3	-	XXX	
T	-	-	-	Category B
Z	-	-	-	
-	3	-	-	
-	2	-	XXX*	
-	2	-	-	Category C
-	1	4	XX	
-	1	3	XX	
-	1	-	-	Category D
-	-	4	-	
-	-	3	X	
-	-	-	XXX	
-	-	-	XX	
-	D/BOD	-	-	

Table XXXI

\* If the substance is non-volatile and insoluble (vapour pressure <1 mm Hg at 200°C and solubility <2g/100 ml at 200°C) otherwise it may be rated as Category C.

The MARPOL categories only render the dangerousness of substances in respect of a water pollution. The hazard to human health through skin contact and inhalation (GESAMP-criterium D) is therefore not being taken into consideration.

Substances which have been evaluated and found to fall within one of the Categories A, B, C or D are listed in Appendix II of Annex II of MARPOL (Appendix III of Annex IV of Helsinki respectively). The Appendix comprises some 180 substances. With the proposed amendment of Annex II

the number of substances listed will increase considerably to some 420 substances, 95 of which being included provisionally.

Other lists of dangerous liquid chemicals are given in the Chemical Tanker Codes

But, because the Codes and the Annex II of MARPOL have different objectives, the lists of substances are not identical. IMO has already agreed that the BCH-Code and the IBC-Code should be extended to cover pollution aspects and the IMO is currently reviewing them to ensure that they are aligned with Annex II when the latter enters into force

. This means that the safety requirements

for each product listed in Chapter VI of the BCH-Code and Chapter 17 of the IBC-Code have to be reviewed and if necessary reassessed taking into account the hazards the product poses to the marine environment.

## LIQUIFIED GASES CARRIED IN BULK

The carriage of liquified gases in bulk is treated in the International Code for the Construction and Equipment of Ships Carrying Liquified Gases in Bulk (IGC-Code) (Res. MSC. 5 ), the Code for the Construction and Equipment of Ships Carrying Liquified Gases in Bulk (Gas Carrier Code) (Res. A. 328 (IX)) and the Code for Existing Ships Carrying Liquified Gases in Bulk (Res. A. 329 (IX)). The IGC-Code will become mandatory under SOLAS Chapter VII Part C from July 1, 1986

The Codes are applicable to liquified gases listed in the Codes (e.g. Chapter 19 of the IGC-Code). The list of the IGC-Code contains 30 substances. Only seven of these products are included in the revised list of noxious liquid substances of MARPOL Annex II, Appendix II and one substance has been found to fall outside the MARPOL Categories. The remaining IGC-Code-substances have not been assessed under MARPOL.

But on the other hand, the Intervention Protocol, 1973 listed 22 liquified gases carried in bulk as being liable to create marine pollution (section 3 of the Annex of the Protocol). These substances have been taken from the Gas Carrier Code.

## SUBSTANCES CARRIED IN PACKAGED FORM

The transport of substances carried in packaged form is treated in the International Maritime Dangerous Goods Code (IMDG-Code), a companion of more than 10.000 pages in five loose leaf volumes. The General Index enumerating the dangerous goods fills nearly 200 pages.

The legal status of the IMDG-Code is that of a recommendation, only, but some 37 countries have adopted the Code fully or partially as national law and another five states are considering adoption

The Code has been designed to assist compliance with the general requirements of SOLAS, Chapter VII. Hence, the striking objective of the IMDG-Code is the safety of ships and persons on board and not the protection of the marine environment. Under MARPOL, Annex III the governments shall issue detailed requirements on the conditions for the transport of harmful substances in packaged forms for preventing or minimizing pollution of the marine environment (Reg. 1 ). With the objective to provide a uniform basis for these national regulations the MEPC laid down basis principles for good practice for packaged substances which are considered to present a serious hazard to the marine environment

(MEPC/Circ. 78; September 19, 1979). These substances shall be called "marine pollutants". Two annexes are attached to the MEPC/Circ. 78. Annex 1 deals with principles concerning the inclusion of pollutants in the IMDG-Code. In section 1 the selection criteria for hazard profiles of substances are given. Annex 2 consists of a list of marine pollutants amounting to some 150 products.

The Sub-Committee on the Carriage of Dangerous Goods (CDG) on its 37th session in May 1985 discussed the matter and proposed

- to add a new section to the General Introduction on the IMDG-Code dealing with marine pollutants
- to include in class 9 of the IMDG-Code (miscellaneous dangerous substances) those harmful substances which do not fall into any other IMO hazard class;
- to modify the IMDG-Code schedules for those dangerous substances which are also harmful. This could include the addition of the words "marine pollutants" in the schedules and for those harmful substances which present a serious hazard to the environment, deletion of inappropriate packagings or the insertion of a requirement that additional protection such as a closed freight container is necessary.

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ANNEX V

History of studies dealing with the maritime traffic  
in the Mediterranean

Sources : Tramed 77 and COST 301 programs

The "TRAMED 77" program, directed by the Commander in Chief for the Mediterranean (CECMED) of the Maritime Prefecture for the third Maritime Region (PREMAR III), had for principal purposes the characterisation of the trade routes in the entire Mediterranean as well as the density of traffic. The data were collected between 1977 and 1979 from all the neighboring countries of the Mediterranean by the Operational Research Group of Toulon (G.R.O.T.). More than 1000 sketches from different countries were collected. The information was especially concerned with petroleum products and liquefied gases which were loaded and unloaded in various Mediterranean ports ; but the collaboration of almost 300 ports located all around the Mediterranean was very fragmentary. Also, it was not possible to inventory the ships transiting in the Mediterranean, i.e. crossing the Mediterranean sea from the Atlantic to the Persian Gulf or Black sea, or vice-versa, without calling any Mediterranean port. The efforts made in order to centralize the data from the TRAMED 77 study, as well as for previous studies called TRACOM 69 and TRACOM 74, enabled certain principal trends for the Mediterranean traffic to be observed ; these trends were again studied in the framework of the European COST 301\* programme (task force 8.50, relating to the Mediterranean).

\* The initials C.O.S.T. are used by the Commission of the European Communities to designate a study program ("Cooperation on Science and Technology") ; the number 301 corresponds to a project defined by the transportation division called "Help for Earth through Maritime Navigation". Code 8.50 designates the task force responsible for studies and trials on maritime traffic in the Mediterranean.



The aim of the Mediterranean program is to study the feasibility of a Mediterranean VTS (Vessel Traffic Services).

An operational center will receive information from existing organizations such as ports authorities or from organizations which have to be created (i.e. local VTS : Tarifa for Gibraltar, Messina, Pertusato for the Strait of Bonifacio, etc...). After the data acquisition, the instant image of traffic will be available. The center will be installed in Genoa and will be known under the initials of MECC (Mediterranean Coordinating Center).

The M.E.C.C. will have to manage an appropriate number of files corresponding to an average of about 4 000 significant ships present at any day within the Mediterranean. This center should be fully operational when this number increases to more than 9 000 messages/day at the same levels of services provided.

When operational, it will be able to interact within the traffic on three levels :

1. Information and assistance to navigation and related marine activities ;
2. Remedial and first aid in case of accidents of various natures ;
3. Enforcement of rules and organisation of traffic, when appropriate and in conformity with national or international rules.

The decision to install a VTS in the Mediterranean is due to the specific character of this sea.

According to Mr. PRUNIERAS, Director of the French Service of Lighthouses and Buoys (Service Technique des Phares et Balises), the "specific character of the Mediterranean is reinforced by the fact that many mediterranean countries will not have, within the foreseeable future, radar monitoring systems of maritime traffic of the same quality as those installed on the coasts of the North Sea."

In order to help in localizing the various Mediterranean routes, the six European satellites NAVSAT which will be launched by 1993 will complement the localization radar.

Data processing will enable a ship's identification, especially for those refusing to do it.

While awaiting the technological advances permitting an even greater precision in this domaine, the Mediterranean is actually equiped with 12 local VTS of which 3 are on a regional importance in the Suez Canal, in Marseilles-Fos and on the Atlantic side of the Strait of Gibraltar ;

However, before achieving this long term objective (in about 10 years), the short term objectives of the COST 301 program are as follows :

- Evaluating the most dangerous sea areas and of the best ways of reducing the risks involved in maritime traffic ;
- Establishing methods for monitoring and assisting dangerous goods carriers with manoeuvring difficulties, in coastal waters, near ports, and in ports.

**N.B.** : Informations on C.O.S.T. 301 are due to A.C.A.M. Leclair, responsible for "CROSSMED" (operational and registral center for salvage and survey ship)

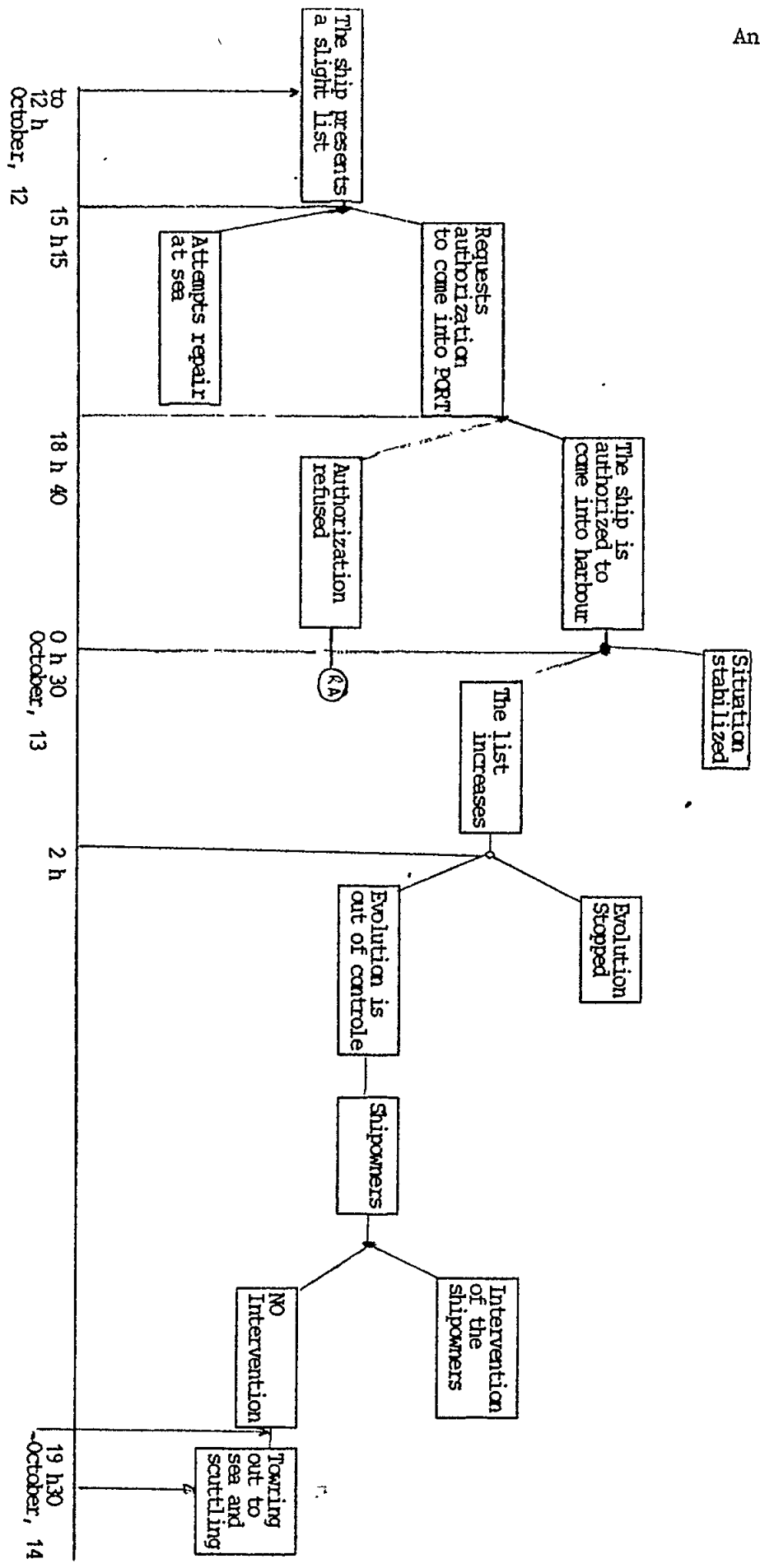
**ANNEX VI**



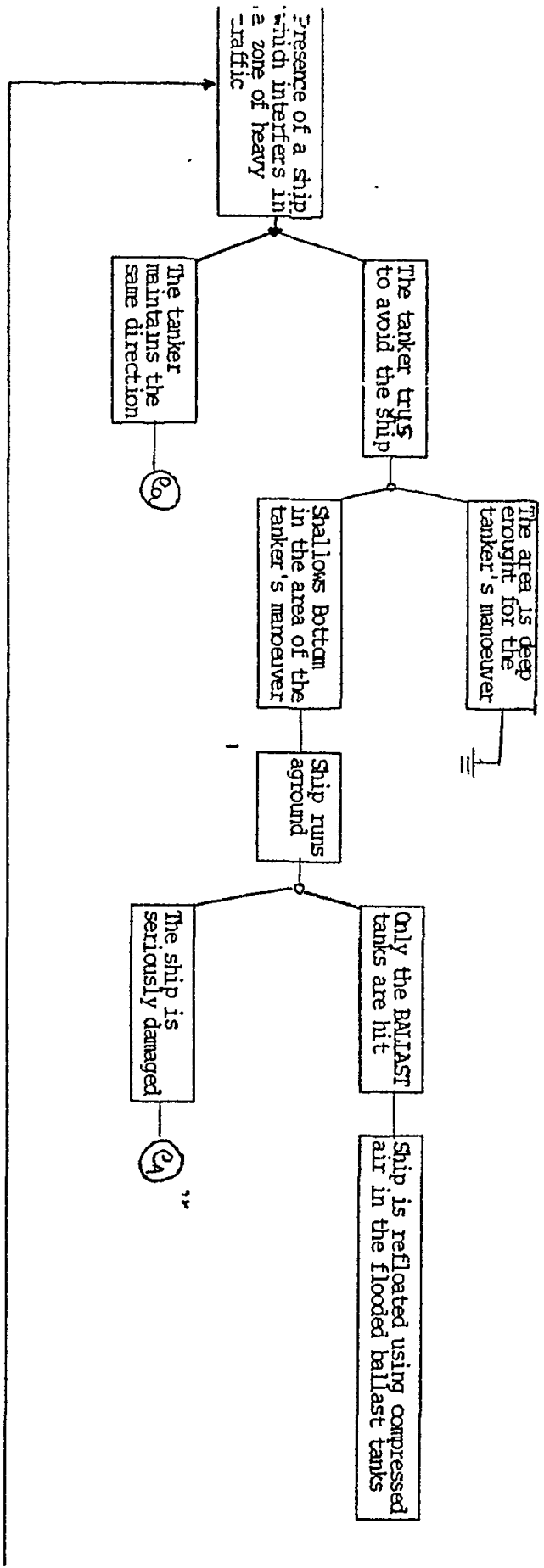
Case studies of Accidents in the Mediterranean Sea :

Tree of Events

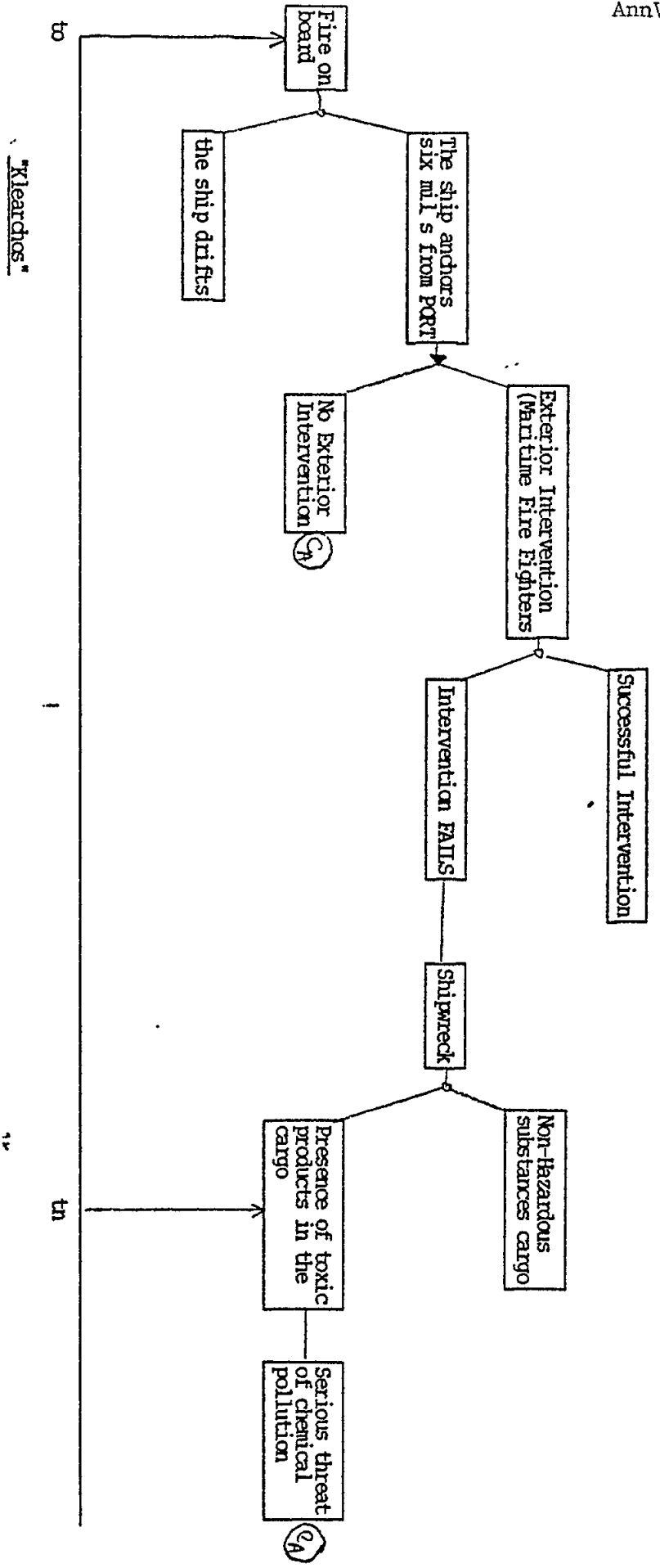
(Source : CEDRE Report, by J. Escande, 1982)



"Gaz East"



"El Paso Paul Kayser"



ANNEX VII

Definition of terms to describe hazard characteristics

INTERNATIONAL MARITIME  
ORGANIZATION



IMO

24 January 1985  
Original : ENGLISH

MARINE ENVIRONMENT PROTECTION  
COMMITTEE - 21 st session  
Agenda item 15

The term "hazard" indicates the probability and potential of a particular substance to cause damage or injury. The following is a brief discussion of the types of hazards which may be encountered:

- 1 **Combustibility:** The ability of a material to burn under normal conditions. For combustion to occur, oxygen, fuel, and an ignition source must be present;
- 2 **Flammability:** The ease with which a material will ignite, either spontaneously from exposure to high temperature, or from exposure to a spark or open flame. The flammability of a material is generally described in terms of a lower flammability level (LFL) and an upper flammability level (UFL). The LFL is the lowest concentration of a fuel-in-air mixture that can be ignited and support combustion and the UFL is the highest concentration that can be ignited and support combustion. Ratios of less than the LFL or of greater than the UFL cannot be ignited;
- 3 **Explosibility:** The ability of a substance, either pure or mixed with other substances, to react rapidly and to produce local high temperatures and to generate large volumes of gases. Generally, when a flammable material is limited to a confined area and ignited, an explosion will result. As with flammability, explosibility is expressed in terms of lower and upper explosive limits;
- 4 **Corrosivity:** The ability of a material to cause electrochemical degradation of metals or alloys due to their reaction with their environment or the destruction of body tissues by acids and bases. The corrosive strength of acids and bases can be relatively indicated by pH values. The pH value of a neutral solution, neither acidic nor basic, is 7. pH values of acids are below 7 and the pH values of bases are above 7;
- 5 **Reactivity:** The ability of a material to change chemically, either by combination, replacement or decomposition. Chemical reactions may be endothermic, requiring heat to maintain them or exothermic, evolving heat;
- 6 **Toxicity:** The ability of a material to cause damage to living tissue, impairment of the central nervous system, severe illness, or in extreme cases death when inhaled, ingested, injected or absorbed by the skin. Toxic substances can generally be divided into two different categories based upon the type of physiological reaction which takes place after entry into the body:
  - .1 **Local:** Action of the toxicant takes place at the point or area of entry or contact. Absorption does not necessarily occur;



- .2 Systemic: Site of action of the toxicant is other than point of contact and presupposes that absorption has taken place. Systemic toxicants can damage an entire organ system, blood forming system or the central nervous system;

Different types of toxic substances which produce a specific effect are:

- .3 Asphyxiant: A substance which interferes with respiration causing insufficient oxygen to sustain life. Simple asphyxiants are inert gases that displace oxygen and dilute the atmospheric oxygen below a level needed to maintain respiration (e.g. CO<sub>2</sub>, methane). Chemical asphyxiants prevent the transport of oxygen from the lungs or transfer of oxygen to the cells;
- .4 Irritant: A substance that inflames moist or mucous surfaces in the pulmonary system, skin or eyes;
- .5 Carcinogen: A substance which causes cancerous growths in living tissues;
- .6 Teratogen: A substance that will produce a physical defect in a developing embryo;
- .7 Mutagen: Any agent capable of inducing mutations in DNA which will produce a permanent, transmissible difference in the characteristics of an offspring from those of the parent;
- 7 Bioaccumulation: Phenomena which cover various processes leading in one way or another to an increase in the concentration of a substance in a living organism;
- 8 Threshold Limit Values: In the United States, the American Conference of Governmental Industrial Hygienists has developed the concept of Threshold Limit Values (TLV's) for use in the working environment. Threshold Limit Values suggest the concentration of a substance to which a normal worker could be exposed without harmful effects. TLV's are expressed as a Time Weighted Average (TWA) for the 8 hour work day and 40 hour work week and as a Short Term Exposure Limit (STEL) for 15 minute excursions above the TWA value.

Use of the TLV requires the identification of the substance or substances of concern. The TLV can then provide a segment of the needed information to assess a hazardous situation. TLV's alone are insufficient for thorough evaluation, and should not be used as a fine line between determining safe and dangerous environments.

The booklet Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment is available from the American Conference of Governmental Industrial Hygienists, P.O. Box 1937, Cincinnati, Ohio 45201 USA. The booklet is updated annually.

ANNEX VIII

Studies on how to respond to discharges  
into the sea of four selected chemicals

Source : Swedish coast guard headquarters  
Bjorn Loostrom  
1980-09-12

Bonn Agreement Working Group (BAWG) is planning to elaborate guidelines for response actions to discharges of chemicals into the sea. To contribute to a basis for the work, studies are here presented on how to respond to discharges into the sea of the following four chemicals which have been selected by BAWG:

· ammonia (evaporator)  
· benzene (floaters)  
· acrylonitrile (dissolver)  
· creosote (sinker)

The conditions specified by BAWG are the following:

- A tanker accident in the North Sea where the complete content of two wing tanks is released.
- Incident location 15 nautical miles from the coast at a water depth of 30 metres.
- Wind direction towards the coast, force 5 Beaufort (=approximately 10 m/s).
- Water current parallel to the coast, speed 1 knot.

The content of two wing tanks in a large chemical tanker is estimated to  $2 \times 1\,000 = 2\,000$  cubic metres.

AMMONIA

on

colorless gas. Its odour is extremely irritating. It is carried at sea under "high pressure and/or low temperature" in liquefied and

liquefied ammonia is 0.68 (at  $-33.4^{\circ}\text{C}$ , boiling point is  $-33.4^{\circ}\text{C}$ . It will dissolve

in the production of e.g. fertilizers, explosives and synthetic fibres.

It is a strong irritant to the eyes and the respiratory organs on wet skin. Higher concentrations than 1.0 % cause severe lung irritation, pulmonary oedema and death. Recommended exposure limits range from 50 ppm during maximum 5 minutes during maximum 30 minutes.

Low. Ammonia is difficult to ignite and does not support a flame. Ammonia can explode under certain conditions (e.g. in enclosed space).

When ammonia is discharged into the sea, a vigorous reaction will start. Under certain conditions the reaction will be extremely vigorous. Especially at a high discharge the reaction will be rather violent ("pressure explosion").

It has been shown that 60% of a massive spill of ammonia on the water will dissolve in the water. In freshwater spills the dissolved part will

be absorbed in water under formation of ammonium ions. The increase of temperature and pH of the solution is a corrosive base which is harmful to aquatic life even in very low concentrations.

Ammonia will vaporize and spread in the air. The evaporation is extremely rapid and liberates (in the form of a dense, white fog of vapour, probably a large fraction of aerosols).

The quantities of liquefied ammonia correspond to a certain amount. At a discharge of this amount on the water will dissolve in the water and 540 tons will be released to the air.

In a tanker accident, 1 360 tons of liquefied ammonia would most likely be released over a period of time ranging from minutes to hours. Immediately after touching the water surface the ammonia will spread into the air and water.

It is difficult in such a case to assess the extension of the area where the ammonia concentration in the air is dangerous to health. The calculations in the literature give results which fall very much apart from each other. The area dangerous to health may extend several nautical miles downwind from the source. Therefore appropriate warnings must be given to seafarers and also to aircraft. The U S Coast Guards Chemical Hazards Response Information System (CHRIS) also gives 2 000 metres as the maximum downwind distance over which a release of 540 tons of ammonia into the air may ignite. However, this assumes worst case weather conditions (steady, low wind) and instantaneous discharge.

The models in literature which describe the dissolution in water of ammonia are established for flowing rivers and streams, and not for the open sea conditions. Experiments have shown that the initial distribution of an ammonia spill on the water only affects the upper layers of the water. However, it is quite probable that the ammonia soon after its distribution in the direction of the water current also will reach the deeper layers.

Ammonia is toxic to aquatic organisms and will cause damage or death at concentrations below 10 ppm (mg/l). 820 tons of dissolved ammonia in water can in theory give 82 million tons of 10 ppm solution. If the depth is 30 metres it is possible (in theory) that a 100 meter wide water area will be affected along a distance of 15 nautical miles in the water current direction.

However the ammonia will spread, it is evident that such a spill will affect large water areas.

### Response

During the response activities three risk zones can be recognized.

Zone I. The fire hazard of ammonia is low but yet it can ignite and the risk zone which for 540 tons of evaporated ammonia can be calculated from CHRIS is 300 x 2 000 metres along the wind direction. This zone must not be entered by ships or engine-driven units which can act as ignition sources. The spill source shall be attacked or inspected from the windward side. Only when the discharge is stopped, the zone can be entered.

Zone II. This is the zone where the concentration of ammonia is too high to breath for unprotected personnel. A rough and preliminary assessment based on data in the literature will give the extension 4 x 15 nautical miles along the wind direction right up to the coast. The zone also comprises all air above these limits. As soon as possible after the accident, warnings must be given to seafarers and aircraft so they do not enter the zone. The zone must be supervised by Coast Guard cutters and aircraft. The zone shall continuously be monitored with gas detection meters. Special.

attention must be given to the coast at the far end of the zone. If the monitoring shows rising concentrations, the zone must immediately be extended further inland. The personnel who enters zone II must wear breathing apparatus and closer to the spill source even full protective suits.

Zone III. This zone is the water area which is affected by the ammonium hydroxide. The extension is very difficult to assess in advance, but from what have been calculated above, it may be very large. The zone shall be defined through monitoring with pH-meters and shall be continuously mapped from these results. This zone shall not be used for fishing and recreational activities. The zone extends along the water current at right angle to the wind direction. The water area where the ammonium hydroxide concentration is highest (close to the spill source) may be treated with sodium dihydrogen phosphate which will neutralize the ammonium hydroxide and reduce the damage of the marine environment. The spreading of the agent can be done with injector jet pipes which are fed with water and allowed to suck directly from the bags with solid sodium dihydrogen phosphate. This method of spreading will transfer the agent as a slurry to the water where it will dissolve and neutralize the ammonium hydroxide. However, the theoretical amount of sodium dihydrogen phosphate will be almost 6 000 tons to fully neutralize the 820 tons of dissolved ammonia. Although the agent is considered completely harmless (it is used in baking powders) such an operation must of course be carried out in consultation with ecological expertise.

BENZENEGeneral information

Benzene is a colourless liquid with gasoline-like odour. The density is 0.88, solubility in water 0.1 %, freezing point +5.5°C, boiling point 80.1°C and vapour pressure 75 mm Hg (at 20°C).

Benzene has a wide use as a solvent and for manufacture of pharmaceutical drugs, dyes and other organic compounds.

Benzene vapour irritates mucous membranes and can also penetrate the skin. Accute exposure to more than 0.3 % benzene in air may cause poisoning with narcotic effects such as restlessness, excitement, convulsions, depression and, if exposure is continued, death through respiratory failure.

Benzene is harmful to aquatic life even in very low concentrations.

Benzene is very flammable and there is an explosion hazard in the presence of an ignition source in a confined space.

When benzene is discharged at sea, it will float and spread out on the surface of the water. Small amounts will dissolve in the water and affect the marine life. Vaporization will start and will proceed comparatively rapidly, especially in warm weather.

Actual discharge

2 000 cubic metres of benzene correspond to a weight of 1 760 tons. In a tanker accident this amount would most likely be released over a period of time ranging from minutes to hours. After touching the water, the benzene will spread out on the water surface and start to vaporize. The vaporization rate is very much dependant on the water temperature. According to CHRIS this amount of benzene will vaporize in 90 minutes at a water temperature of 20°C. At lower temperatures the vaporization time will be greater. Below +5.5°C the benzene will freeze and form solid layers which still float (density 0.90).

As the solubility of benzene in water is very slight (0.1%) a rather small part of the spill will be dissolved. It will affect only the water areas close to the pathway of the spill. But the toxicity of benzene is high enough to cause considerable damage to the marine life in this location.

Response

The vaporized benzene gives rise to a zone where the atmosphere is dangerous to health. It is difficult to assess the extension of this zone but it may be reasonable to expect an area of one or two nautical miles in the wind direction from the polluted water site. As soon as possible after the discharge it is necessary to monitor and map this zone continuously by gas detection meters. Seafarers and aircraft must be warned and the surrounding area must be patrolled by Coast Guard cutters and aircraft. The zone shall be entered only by personnel equipped with breathing apparatus. Close to the spill they shall also wear full protective suits.

In the vicinity of the spill the fire risk shall be monitored with explosimeters. Relevant safety measures shall be taken to restrict access by ships and engine-driven units which contain ignition sources. The spill source and the floating spill itself shall be attacked or inspected from the windward side. Entry of this area shall be restricted as far as possible for all personnel due to the high flammability of benzene. This precaution does apply especially for conditions when the vaporization of benzene is too high to get time for meaningful skimming operations.

The water area under the pathway of the benzene slick shall be monitored by sampling and analyses during the course of the response operation and afterwards. This area shall be mapped in order to make an assessment of the environmental damage possible. However the amount of dissolved benzene is too small to make any combating action possible within the water phase.

In summertime when the water temperature is greater than  $+10^{\circ}\text{C}$  it may be difficult to pick any benzene before it evaporates. But in lower temperatures and especially when the benzene is solid (below  $+5.5^{\circ}\text{C}$ ) it can probably be taken up by belt skimmers or rotating disc skimmers. The operations must be carried out under strict safety precautions. Working personnel must be equipped with breathing apparatus and full protective suits. The work must be continuously monitored with explosimeters.

#### Disposal

Recovered benzene (mixed with water) shall be sent to a refinery or disposal plant for purification by means of distillation.



## ACRYLONITRILE

### General information

Acrylonitrile is a colourless to light yellow liquid with a sweet, mildly irritating odour. The density is 0.81, solubility in water 6.8 % (at 20°C), freezing point -83.5°C, boiling point 77.3°C and vapour pressure 100 mm Hg (at 20°C).

Acrylonitrile is used for manufacture of e.g. plastics, synthetic fibres and adhesives.

Acrylonitrile vapour is highly toxic and cause (from low to high concentration) weakness, headache, nausea, abdominal pain, asphyxia and death.

Acrylonitrile is harmful to aquatic life even in very low concentrations.

Acrylonitrile is flammable and can explode in an enclosed space in the presence of an ignition source. The combustion products of burning acrylonitrile are extremely toxic.

When acrylonitrile is discharged at sea it will initially float and spread out and then dissolve into the water. Before dissolution some amount will vaporize. The degree of vaporization is due to environmental factors such as water temperature and wind force.

### Actual discharge

2 000 cubic metres of acrylonitrile correspond to a weight of 1 620 tons. In a tanker accident this amount would most likely be released over a period of time ranging from minutes to hours. After touching the water the acrylonitrile will spread out on the water surface and start to vaporize into the air and dissolve into the water. The values of vapor pressure and solubility are high enough to make the acrylonitrile vanish from the water surface in a comparatively short time.

Due to the high solubility and high toxicity of acrylonitrile the marine life close to the spill source will be considerably damaged. The spreading of the dissolved acrylonitrile will affect large water areas. Acrylonitrile is harmful to many marine organisms at concentrations of 10 ppm. 1 200 tons of acrylonitrile will give a theoretical amount of 120 million tons of 10 ppm solution. If the depth is 30 metres it is possible (in theory) that a 100 meter wide area will be affected along a distance of 22 nautical miles in the water current direction.

### Response

Three risk zones can be recognized during the response activities.

Zone 1. Near the spill source there is a zone where the fire risk is high. It is difficult to predict the extension of the

zone and it cannot be monitored with explosimeters as they are not calibrated for acrylonitrile. But it is reasonable to consider an initial area of half a nautical mile in the wind direction from the undissolved slick. The zone must not be entered by ships or engine driven units which can act as ignition sources. The spill source and the slick shall be attacked or inspected from the windward side.

Zone II. This is the zone where the vapors are hazardous to unprotected personnel. It is difficult to assess the extension of the zone because a great part of the acrylonitrile dissolves into the water. It is possible that the zone will extend to a distance of one or two nautical miles along the wind direction. The extension of the zone must be continuously monitored by gas detection meters. Seafarers and aircraft must be warned and the surrounding area must be patrolled by Coast Guard cutters and aircraft. The zone shall be entered only by personnel equipped with breathing apparatus. Close to the spill they shall also wear full protective suits.

Zone III. This zone is the water area which is affected by the dissolved acrylonitrile. From what has been calculated above the extension of the zone may be very large. The zone shall be continuously mapped through sampling and analyses. This zone shall not be used for fishing and recreational activities. The zone extends along the water current at right angle to the wind direction.

The spreading, vaporization and dissolution of the acrylonitrile will make the spill very difficult to recover. The high toxicity and the fire risk will make the situation still worse. Probably the best way is only to supervise the zones. It is probably not reasonable to treat the polluted waters with any treating agent. Possibly it may be sensible to help local concentrations of acrylonitrile to disperse by agitating the area with water sprays or propeller blasts from cutters.

## CREOSOTE

### General information

The kind of creosote which is most often bulk transported at sea is the coal tar creosote (creosote oil) which is a distillation product of coal tar which in turn is derived by carbonization (destructive distillation) of bituminous coal. Creosote is a complex mixture of aromatic hydrocarbons and phenols which is used mainly for impregnating wood. It is a yellowish to dark green-brown, oily liquid. The odour is tar-like.

The density is usually 1.05 - 1.09 (compared to sea water 1.03). It is practically insoluble in water. The freezing point is generally below 0°C but sometimes higher (up to +30°C). The boiling point is generally 190-240°C. The vapour pressure is generally below 1 mm Hg (at 20°C).

Creosote is irritating to skin and eyes. It is a recognized carcinogen of skin and an experimental carcinogen of the lungs - but this probably pertain to repeated or prolonged contacts.

The effect of low concentrations of creosote on aquatic life is unknown but probably will both acute and chronic damage appear at discharges at sea. Creosote will be fouling on shorelines.

The fire hazard is moderate when exposed to heat or flame.

The density of creosote is very close to and most often slightly greater than the density of sea water. At a discharge at sea creosote will sink slowly to the bottom.

### Actual discharge

2 000 cubic metres of creosote correspond to a weight of about 2 140 tons. In a tanker accident this amount would most likely be released over a period of time ranging from minutes to hours. After touching the water the creosote will follow the water current and slowly sink to the bottom. It is very difficult to predict where it will reach the bottom e.g. at a water current of 1 knot and a water depth of 30 metres. The creosote will probably be spread on the bottom in the direction of the water current.

The solubility of creosote is very slight. Exact solubility data are not given in the literature. But the solubility is probably enough for very small amounts of toxic components to be released in soluble state into the water and affect the marine life, especially on and close to the bottom sediments.

### Response

The polluted bottom area must be mapped carefully. This is best done visually by divers which must be equipped with completely tight dry diving suits. The bottom-lying creosote can then be dredged with a hydraulic dredge under the supervision of divers. A mechanical dredge or a hydraulic dredge with a mechanical cutterhead should not be used as they cause turbulence at the bottom that would spread the creosote

still more and cause greater damage to the marine environment. In order to recover as much as possible of the creosote, a great part of bottom sediment must be dredged together with the creosote.

The dredged material shall be transferred to barges and transported to a harbour which has facilities to receive it. Personnel which are working close to the dredge material must be equipped with breathing apparatus and protective suits.

#### Disposal

The sediment material should be transported to disposal sites for long term storage, for future use in e.g. roadbed filling!

ANNEX IX

Lecturers



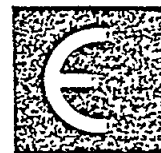
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EUROPEAN COMMUNITIES



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EUROPEAN COMMUNITIES

Ir. P. Bockholts

TNO  
Division of Technology for Society  
Dept. of Industrial Safety

Response / Preparation:  
Support of Hazard identification and decision making.

K.J. Bolt

Directorate General Shipping  
and Maritime Affairs  
Dept. P.N.M.

Hazard awareness:  
Management objectives for a  
response organisation.  
Hazard awareness / Prevention:  
Regulations, State of the art,  
White spots, Limitations.

B.H. Brinkhuis

Depot Milieubeheer B.V.

Preparation / Response tools  
Demonstration clean-up methods.  
Field excursions.  
Industrial clean-up capabilities.  
Cases.

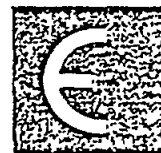
Th.A. Buys

Depot Milieubeheer B.V.

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Demonstration clean-up methods.  
Field excursions.  
Industrial clean-up capabilities.  
Cases.



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Dr. D. Cormack

Warren Spring Laboratories  
Dept. of Industry

Preparation:  
Hazard assessment and  
identification of packed and  
hazardous materials.  
Control and reduction of  
effects.  
Conclusions for objectives.  
Discussions.

Capt. A. van Eden

Rijkswaterstaat  
North Sea Directorate

Introduction:  
Official opening of the course.  
Communication:  
Response organisation  
Rijkswaterstaat

H.Ph. Groenewoud

Depot Milieubeheer B.V.

Preparation / Response tools  
Demonstration clean-up methods.  
Field excursions.  
Industrial clean-up capabi-  
lities.  
Cases.

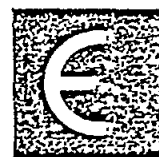
G.M. Hadfield

Dow Chemical (Nederland) BV  
Manager Europe Safety Security  
Loss Prevention

Preparation / Communication:  
Presentation DOW.



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EUROPEAN COMMUNITIES

M.H. de Heer

Chemical Laboratory "Dr. A. Verwey"  
Analysts and Consulting Chemists  
Samplers and Weighers  
Bulkoil-surveyors

Hazard awareness:  
Properties of hazardous  
materials.  
Preparation:  
Hazardous materials exposure  
risks.  
Measurement limitations.  
Exposure risks of personnel.  
Personnel protection.

Dr. R.P.W.M. Jacobs

Nederlandse Aardolie Mij.  
Environmental Dept.

Hazard awareness:  
Management objectives for a  
response organisation.

Drs. B.M.G. Jansen

Central Environmental Protection  
Agency (Rijnmond) Rotterdam

Response organization:  
Rijnmond area.

Ing. W. Koops

Rijkswaterstaat  
North Sea Directorate

Hazard awareness:  
Hazard material spills. Cases.  
Response / Preparation:  
General steps in preparation  
Preparation:  
Conclusions for objectives.  
Discussions.

B. Looström

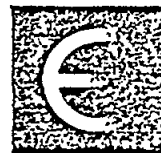
Swedish Coast Guard

Preparation:  
Hazard assessment and  
identification of packed  
hazardous materials.  
Control and reduction of  
effects.  
Conclusions for objectives.  
Discussions.





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Dipl. Ing. P. Nimptsch

BASF

Response:  
Industrial Response activity.  
Philosophy, Organisation.  
Demonstrations of Industrial  
Response.  
Techniques.

E. Norman

National Foam

Preparation / Response tools:  
The control of Fire and  
Hazardous Vapours by water and  
foam techniques.  
Principles.

M. Renson

Commission of European Communities  
Representative

Introduction:  
The Community Action Plan of  
Harmfull Substances Spilled at  
Sea.

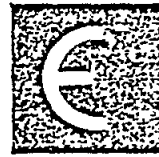
Ing. E.W. Rocco

Dow Chemical (Nederland) BV  
Director Governmental Relations  
Materials  
Management Dow Europe

Preparation / Communication:  
Presentation DOW.



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THE COMMISSION OF THE  
EUROPEAN COMMUNITIES

J.A.C. van Rooy

Smit Tak International Ocean Towage  
& Salvage Co.  
Salvage Superintendent

Hazard awareness:  
Management objectives for a  
response organisation.

Ir. T. Verhoeff

Rotterdam International Safety Centre  
Course director

Introduction:  
Aim and outline of the course.  
Aim of student activities.  
Domestic affairs.  
Preparation:  
Evaluation of week one.  
Conclusions for objectives.  
Discussions.

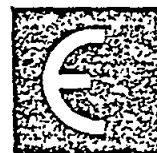
Drs. F.W.J. Vos

Rotterdam International Safety Centre  
Course director

Introduction:  
Aim and outline of the course.  
Aim of student activities.  
Domestic affairs.  
Incident management.  
Response:  
Response capabilities  
evaluation.  
Response / Preparation:  
Objectives for "tool"  
development.  
Preparation:  
Evaluation of week one.  
Conclusions for objectives.  
Discussions.  
Recapitulation / Evaluation:  
Recapitulation of syndicat  
activities.  
General "objectives".



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THE COMMISSION OF THE  
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Salvage Superintendent

Hazard awareness:  
Hazard materials spills. Cases.  
Management objectives for a  
response organisation.

A.J.W. Wolters

Municipal Port Management  
Port of Rotterdam  
Deputy Harbourmaster  
Operational Safety

Response organization:  
Port of Rotterdam

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**GLOSSARY OF ABBREVIATIONS (not United Nations)**

- BAWG : Bonn Agreement Working Group
- CECMED : Commandement en chef pour la Méditerranée (France)
- CEDRE : Centre de Documentation, de Recherche et  
d'Expérimentations sur les Pollutions Accidentelles  
des Eaux. (France)
- CEPPOL : Commission d'Etudes Pratiques de Lutte Anti-Pollution  
(France)
- CETENA : "Italian ship Research Centre".
- CHRIS : Chemical Hazards Response Information System.
- COST : Cooperation on Science and Technology (See Annex V)
- CROSSMED : Centre Régional Opérationnel de Surveillance et de  
Sauvetage pour la Méditerranée. (France)
- DMI : Danish Maritime Institute
- DPNM : Direction des Ports et de la Navigation Maritime  
(France)
- EPA : Environmental Protection Agency.
- FSSH : Forschungsstelle für die Seeschifffahrt zu Hamburg E.V -  
Hamburg Maritime Research (FRG).
- HACS : Hazards Assessment Computer System.

IFP : Institut Français du Pétrole

IFREMER : Institut Français de Recherche pour l'Exploitation de  
la Mer. (France)

INSERM : Institut National de la Santé et de la Recherche  
Médicale (France).

IRCHA : Institut National de Recherches Chimiques Appliquées  
(France).

MARIN : Maritime Research Institute Netherlands

PREMAR III: Préfecture Maritime III<sup>e</sup> région (France)

RISC : Rotterdam International Safety Centre

SCG : Swedish Coast Guard

SHOM : Service hydrographique et océanographique de la Marine  
(France)

USCG : United States Coast Guard.