

Hazard Assessment for Chemicals Carried by Ships

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Summary

The safety and pollution hazards of noxious substances transported by ships are evaluated and classified according to regulations and procedures developed by the International Maritime Organization (IMO). For noxious liquid substances shipped under regulations of MARPOL Annex II and the “chemical tanker code” a scientific evaluation by GESAMP, a group of United Nations’ experts, is mandatory. The principles, the rationale and the results of GESAMP’s hazard assessment procedure will be presented. The biological accumulation and degradation in the environment, the aquatic toxicity, the acute and long-term hazards for humans and the behaviour of the substances in the sea are evaluated. The resulting classifications are used for assigning carriage requirements for bulk liquids. The hazards of packaged dangerous goods are often classified by the producer alone. However, the rules are given by the IMO and this organization assigns emergency schedules for fire and spillage for all cargoes. Assessments, classifications and guidance documents are updated and published as IMO documents on a regular basis. The potential use of these IMO documents for risk assessments and risk communication during an accident or a spill involving chemicals will be outlined. Some background knowledge can help to use the scientific and technical information for early advice and a first risk assessment during response at sea.

Introduction

Shipping chemicals in tankships has a number of environmental effects (see 3) although ships are smaller than most oil tankers, safer with less spilled cargoes than those from oil tankers (see 4). However, many cargoes are more toxic than mineral oil. Under the chemicals shipped in containers or tanks as cargo transport units, some of the most toxic industrially produced chemicals are shipped. Therefore, before shipping any cargo, the hazardous properties of the materials should be known. This is clearly a responsibility for the consignor, who should get such information from the manufacturer.

As safety and environmental protection is concerned, the global maritime transport of chemicals is regulated by different International Maritime Organization (IMO) Conventions and Codes (see 5). The safety and pollution hazards of materials transported by ships are evaluated and classified according to these regulations and the procedures developed by the International Maritime Organization (for details see 7).

According to the Law of the Sea, regulations approved by IMO even if not ratified by a coastal state have to be accepted or even followed in maritime traffic by this state. With this legal background, the IMO had become one of the globally most important organizations for hazard classification of chemicals.

Today, most hazard definitions are internationally harmonized by a global system of hazard classification through the United Nations.

The Role of the UN

In 1992, the Earth Summit in Rio de Janeiro (UNCED), decided to establish a Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Aspects of health and environmental hazards were developed by the Organisation for Economic Co-operation and Development (OECD) on behalf of a global Programme for the Sound Management of Chemicals established after the Conference. The International Labour Organization (ILO) as well as many other United Nations organizations were involved. In 2001, a special Committee under the United Nations Economic and Social Council (ECOSOC) was established to oversee the programme and the resulting guidelines. The system was published in 2002 with the 2nd edition printed in 2007 (15).

In 1953, the United Nations Economic and Social Council (ECOSOC) created within the Economic Council for Europe, the UN Committee of Experts on the Transport of Dangerous Goods (UN CETDG). This Committee elaborated the first internationally recognized classification and labelling system for the purpose of transporting dangerous goods. It was first published in 1956 as the UN Recommendations on the Transport of Dangerous Goods, the TDG or "Orange Book" (16). With the decision to align the GHS work and the work with the UN Economic and Social Council (ECOSOC) a push to global harmonisation was created. The UN Model Regulation integrated the GHS quite fast.

The Role of GESAMP and IMO

Scientific advice on risk and hazard evaluation for IMO is prepared by GESAMP. It was therefore GESAMP, that was asked in the late 1990's to review the scientific guidelines for classification of chemicals transported by bulk that had been developed more than twenty years ago. The new revised guidelines for the evaluation of chemicals transport by ships were finished at the same time when the GHS was accepted.

To bring these revised guidance into force and revise IMO's safety and environmental protection legislation accordingly, the IMO decided to re-evaluate about 800 chemicals that were transported by chemical tankers at that time. IMO became the first international organization that evaluated and classified a large number of chemicals according to the GHS. In addition to the criteria defined for the GHS, GESAMP developed further procedures for the evaluation of substances harmful to the marine environment to cover all hazards as defined by the International Convention for the Prevention of Pollution from Ships (MARPOL): "...any substance which, if introduced 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, and includes any substance subject to control by the present Convention..." (11).

Based on the evaluations and hazard ratings created by GESAMP, IMO developed a classification system for bulk cargoes within an international chemicals tanker code, the IBC Code (3) both under safety aspects (SOLAS, see 12) and environmental protection aspects (MARPOL, see 11). As in similar regulations, risk classifications fall into three categories (for comparisons see 8), ship types 1-2-3, pollution categories X-Y-Z, etc. The minimum carriage requirements for safety and pollution reasons are defined and can in general be based on the GESAMP Hazard Profile.

GESAMP's Hazard Evaluation

GESAMP which is the abbreviation for “IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection”, an United Nations’ inter-organizational body. It was created in 1969 for UN advice and prepared topics on marine protection issues for the Stockholm Conference, the first of a series of conferences the latest the Rio de Janeiro and Johannesburg summits. In the early 1970s, GESAMP developed a hazard evaluation and classification concept for liquid bulk cargoes under the MARPOL Convention (for history see 9).

A panel of experts from GESAMP, IMO, industry and Greenpeace (for the non-governmental organisations) developed principles for a basic revision in 1995 and GESAMP presented a first detailed draft of new hazard evaluation criteria in 1998. The reasons for amending the criteria in the late 1990s were threefold:

- The criteria were based on the art of science in the late 1960s.
- The hazards covered acute effects but no long-term effects to aquatic organisms.
- The introduction of the GHS had been decided for all United Nations’ work.

After approval by IMO, the evaluation of 800 chemicals transported in tankships started. The final official Guidance “Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships” was published in 2002 (1). The hazard profiles of all chemicals transported in bulk under MARPOL and the chemical tanker code (IBC Code) could be finalized in 2006.

The GESAMP Hazard Profile for chemicals

For each chemical 14 hazards are evaluated. An additional hazard assessment for people working in spill exposed coastal zones is presented. These 13 hazards are shown in columns for about 900 chemicals resulting in a table which is published by IMO on a yearly basis (for an up-to-date list see 10):

ANNEX 4 - GESAMP/EHS COMPOSITE LIST

New GESAMP Hazard Profiles																
Name	EHS TRN	A1a	A1b	A1	A2	B1	B2	C1	C2	C3	D1	D2	D3	E1	E2	E3
Acetic acid	13	0	0	0	R	1	NI	1	1	1	3C	3		NI	D	3
	64	RTECS No. AF1225000						CAS No.						64-19-7		
Acetic anhydride	12	0	0	0	R	1	NI	1	0	2	3	3	A	NI	D	3
	63	RTECS No. AK1925000						CAS No.						108-24-7		
Acetochlor	2047	3	2	2	NR	4	NI	1	0	(1)	0	0	3	NI	S	2
	66	RTECS No. AB5457000						CAS No.						34256-82-1		
Acetone	15	0	0	0	R	0	0	0	0	0	1	2		NI	DE	1
	67	RTECS No. AL3150000						CAS No.						67-64-1		
Acetone cyanohydrin	14	0	0	0	R	4	NI	3	4	3	(3)	(3)		NI	D	3
	68	RTECS No. OD9275000						CAS No.						75-86-3		
Acetonitrile	16	0	0	0	R	1	NI	1	1	2	1	2		NI	D	1
	69	RTECS No. AL7700000						CAS No.						75-05-8		
Acetonitrile (Low purity grade)	2333	0	NI	0	R	3	NI	1	1	2	1	2		NI	D	2
	2876	RTECS No.						CAS No.								
Acid oil miscella from soyabean, corn (maize) and sunflower oil refining	2306	(0)	NI	(0)	(R)	(0)	NI	0	(0)	(1)	(1)	1		NI	Fp	2
	1036	RTECS No.						CAS No.								

The following hazards are evaluated (see overview in appendix 1):

Within column A1, the prediction of the tendency of a substance to bioaccumulate in aquatic organisms is shown. The relevant measurements are the Octanol/water partition coefficient (log Pow) and the Bioconcentration factor (BCF) in fish. A rating of “≤4” alerts about accumulation in the marine environment after a spill.

Within column A2, the potential of substance to be degraded in the aquatic environment is evaluated. Substances rated as “NR” are not biodegradable within 28 days and thus will stay in the marine water.

Within column B1, the potential to kill aquatic organisms in a short time is evaluated. The acute aquatic toxicity is tested in fish, crustacea (daphnia) and algae for 72-96 hours. A rating of “ ≥ 3 ” means that more than 50% of all organisms will be killed by the chemical at a concentration of 10 grams per cubic meter or even below. A rating of “6” would show, that less than 0.01 grams of the chemical diluted in one cubic meter of water would have that effect. The level of concern after spillage has to be evaluated together with the volume spilled.

Within column B 2, the long-term or chronic toxicity to aquatic organisms is evaluated after being tested in fish or crustacea (daphnia) for 28 days. The level of concern after a spillage has to be evaluated together with biodegradation and behaviour in the environment (columns A2 and E2) in particular.

Within column C, the potential for poisoning humans is evaluated, mostly by rat experiments oder human experience: Under C1 via swallowing, under C2 via skin contact and under via inhalation toxicity. Ratings of “ ≤ 2 ” are assigned to those chemicals which would be labelled with skull & bones when packed and pose a strong and immediate hazard.

Within column D1 the hazard for the skin is evaluated. Ratings of “2” are assigned to chemicals that will show clear irritation, rating of “3” will destruct the skin or eyes. Vapours of such chemicals or aerosols of mixtures with sea water can severely obstruct the respiratory system.

Within column D3, the potential long term health effects to men are evaluated. The letters assigned define the specific effects

- C for substances that may create tumors (carcinogenicity)
 - M for substances that may interact with genes (mutagenicity)
 - R for substances that have an effect on the reproduction of men or women, or which are dangerous for the fetus or the baby
 - S for substances that create allergies
 - A for substances that pose an aspiration hazard, a lung damage after swallowing.
- Further specific toxic effects are rated as “T”, “L”, “N” or “I”.

Within column E1, the interference with fisheries is covered. The rating of “T” is associated with those chemicals that influence the smell or taste of fish after spillage. However, it should be noted that there is no further testing and evaluation of this hazard. For the background of this development (see 6).

Within column E2, the behavior of chemicals in or on the sea is estimated. Following classifications are assigned:

- F Floater, not likely to evaporate or to dissolve
- Fp Persistent Floater, likely to reach coastal areas persisting on the sea
- S Sinker, depositing on the sea bed
- D Dissolver, dilutes in water
- E Evaporator, goes into the air

This column had been introduced by GESAMP on request by IMO after spillages of non-toxic white oils, in particular vegetable oils like palm oil, polluted coastal regions and killed birds

(for background see 2). Liquids rated with “Fp” and those liquids with long term health effects rated “F” have to be transported in double hull ships. Spills of such liquids do have similar effects like spills of mineral oils.

Within column E3, an evacuation advice is given based on the combination of hazardous properties that may create hazards for fishermen, tourists and spill responders. A number of countries in Asia and Africa had asked GESAMP specifically for such advice for all chemicals other than mineral oil transported in tankships.

Depending on the dilution and the behaviour in the water (see column E2) a rating of “2” and above could ask for the use of specific personal protection for spill responders in a worst case situation.

3 Warning issued leading to the closure of amenities

2 Warning issued and possible closure of amenities

1 Warning issued but no closure of amenities

0 None

The classification of ca. 900 chemicals according to this evaluation had been circulated in e.g. Germany officially and could be used for first advice if no detailed knowledge about a specific spill situation is known.

Transport of packaged dangerous goods

The International Maritime Organization (IMO) updates regularly its global regulation for the transport of packages dangerous goods the International Dangerous Goods Code (IMDG Code). Since many years, as far as the criteria and the labelling procedures are concerned, the IMO rules are based on the UN Model Regulation (the Orange Book or TDG regulation) except those for marine pollutants. However, the GHS included work on harmonization of the hazard to the aquatic environment, too. The last version of the IMDG Code is strictly based on the UN Model Regulation.

Based on these criteria the hazards are used for assigning hazard classes with transport labels (see appendix 2). The classification has direct implications for packaging, stowage on board and transport declaration. More than 90% of all such cargoes are packed or filled into containers. Most relevant for spill response after container loss from vessels are the labels for poisonous products, corrosive liquids and the marker for environmentally hazardous substances (marine pollutants).

Annex III of the International Convention for the Prevention of Pollution from Ships (MARPOL) lays down a set of rules for Marine Pollutants including marking, labelling (marking), documentation and stowage. From a practical standpoint, these regulations are an integral part of the IMDG Code. According to MARPOL, reports shall be made by the fastest telecommunication channels when a discharge or probable discharge involves harmful substances in packed form including containers. Marine Pollutants are also listed by the Protocol related to Interventions on the High Seas of Pollution by Substances other than Oil. Therefore, the identification of a cargo as marine pollutant and the labelling with that marker has a direct influence on the information about cargoes in case of an incident.

However, in case of a spill the hazard identification with the corresponding labelling can only offer a warning. The risk for responders on sea or at the coast is furthermore in particular depending on the behaviour of the substances in or on the water and the concentration at the spill site. It has to be known that the long-term hazard to men is not covered by this hazard classification and labelling system.

IMO's Emergency Schedules

As fire or leakage on board ships could happen, a guidance document contains information about fire fighting and spillage response on deck or in enclosed spaces. Recommended procedures are listed in the EmS Guide, a supplement to the IMDG Code (14). As a specific UN number is assigned to each and every dangerous cargo listed in the IMDG Code, there are references between these UN numbers and the Emergency Schedules. The UN numbers are shown in shipping documents and are labelled on cargo units.

26 Emergency Schedules for spillage give structured information for all dangerous cargoes regulated by the IMDG Code. A group of experts worked several years to create this guide which is updated every two years. The spillage schedules contain following information (see example under appendix 3):

- General comments on the risks and personal protection measures for spill responders
- Guidance for small spillages from single packages and large spillages from cargo transport units on deck
- Guidance for small spillages from single packages and large spillages from cargo transport units under deck (in enclosed spaces)
- Special advice for specific cargoes assigned to this schedule

The EmS Guide could be used by spill responders off board, too. Reference should be made to large spillages on deck when using the guide at the coast. Although the hazard classification by the IMDG Code does not distinguish between liquids floating on water and those which are water-soluble, the spillage schedules try to do. However, in many cases specific data on the behaviour of substances in the water are needed. In practice, in many cases evaluation by GESAMP can be used as many chemicals transported in tank container are also transported by chemical tankship, thus requiring an evaluation by GESAMP.

Conclusion: Potential uses of IMO's classifications for spill response

The information provided by hazard classification of packaged goods as well as the hazard evaluation of liquids transported in bulk can be used as scientific and technical information for early advice during spill response. Moreover, the hazard profiles for liquids developed by GESAMP show basic information for a first risk assessment when starting spill response. Although further data - in particular on the concentration in the environment – are needed for a comprehensive risk assessment at the site and adequate personal protection for spill responders, column E3 of the GESAMP Hazard Profile and the EmS Spillage Schedule offer basic guidance for fighting spillages involving hazardous and noxious substances. The mentioned IMO documents should therefore be available for maritime emergencies.

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Disclaimer

The views and conclusions expressed are those of the author alone and do not reflect decisions, policies or views of any organisation concerned.

Further Reading

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Appendix 1

The Revised GESAMP Hazard Profile

Columns A & B Aquatic environment					
Numerical Rating	A Bioaccumulation and Biodegradation			B Aquatic Toxicity	
	A 1 Bioaccumulation		A 2 Biodegradation	B 1 Acute Toxicity LC/EC/IC ₅₀ (mg/l)	B 2 Chronic Toxicity NOEC (mg/l)
	log Pow	BCF			
0	<1 or > ca. 7	not measurable	R: readily biodegradable NR: not readily biodegradable	>1000	>1
1	≥1- <2	≥1- <10		>100- ≤1000	>0.1- ≤1
2	>2- <3	>10- <100		>10- ≤100	>0.01- <0.1
3	≥3- >4	≥100- <500		>1- ≤10	>0.001- ≤0.01
4	>4- <5	>500- <4000		>0.1- ≤1	<0.001
5	≥5	≥4000		>0.01- <0.1	
6				<0.01	

Columns C & D Human Health (Toxic Effects to Mammals)						
Numerical Rating	C Acute Mammalian Toxicity			D Irritation, Corrosion & Long term Health Effects		
	C 1 Oral Toxicity LD ₅₀ (mg/kg)	C 2 Percutaneous Toxicity LD ₅₀ (mg/kg)	C 3 Inhalation Toxicity LC ₅₀ (mg/l)	D 1 Skin irritation & corrosion	D 2 Eye irritation & corrosion	D 3 Long term health effects
0	>2000	>2000	>20	not irritating	not irritating	C - Carcinogen M - Mutagenic R - Reprotoxic S - Sensitising A - Aspiration haz. T - Target organ systemic toxicity L - Lung injury N - Neurotoxic I - Immunotoxic
1	>300-≤2000	>1000- <2000	>10-≤20	mildly irritating	mildly irritating	
2	>50-≤300	>200-≤1000	>2-≤10	irritating	irritating	
3	>5-≤50	>50-≤200	>0.5-≤2	severely irritating or corrosive 3A Corr. (≤4hr) 3B Corr. (≤1hr) 3C Corr. (≤3m)	severely irritating	
4	≤5	≤50	≤0.5			

Column E Interference with other uses of the sea			
E 1 Tainting	E 2 Physical effects on Wildlife & benthic habitats	Numerical rating	E 3 Interference with Coastal Amenities
NT: not tainting (tested) T: tainting test positive	Fp : Persistent Floater F : Floater S : Sinking Substances	0	no interference <i>no warning</i>
		1	slightly objectionable <i>warning, no closure of amenity</i>
		2	moderately objectionable <i>possible closure of amenity</i>
		3	highly objectionable <i>closure of amenity</i>

Appendix 2

Important hazard labels for packaged goods

Toxicity to aquatic organisms
(Marine Pollutant)



Poisonous for humans



Corrosiveness to skin or material



Flammability



Chemical reactivity or explosion, e.g.



Appendix 3

SPILLAGE SCHEDULE Echo

S-E

FLAMMABLE LIQUIDS, FLOATING ON WATER

General comments		<p>Avoid sources of ignition (e.g. naked lights, unprotected light bulbs, electric handtools). Liquid is flammable and spillage may evolve flammable vapours.</p> <p>Wear suitable protective clothing and self-contained breathing apparatus.</p> <p>Stop leak if practicable.</p> <p>In general, substances covered under this schedule will have fuel oil like properties. They are immiscible with water and are liable to float on the surface of water. The use of inert absorbent material, as used in machinery spaces, is appropriate in all cases. For sticky liquids, shovels may be used, preferably shovels made of non-sparking or non-ferrous material.</p> <p>You may use light oil or soap-like products (surfactants) to clean small areas. Clean the area thoroughly because of the flammability hazard.</p> <p>Any pumping of spilled liquid overboard will create an oil spill on the sea surface. In this case: Contact coastal authorities.</p> <p>Report discharge overboard according to MARPOL reporting requirements.</p>
Spillage on deck	Packages (small spillage)	Collect spillage in oil drums, metal boxes or salvage packagings. You may use inert absorbent material.
	Cargo Transport Units (large spillage)	<p>Restrict flow of leakage to an enclosed area (e.g. by diking with inert material or cement).</p> <p>Collect spillage in oil drums, metal boxes or salvage packagings. You may use inert absorbent material.</p> <p>Otherwise, wash overboard with copious quantities of water.</p>
Spillage under deck	Packages (small spillage)	<p>Shut off possible sources of ignition in the space. Provide adequate ventilation. Do not enter space without self-contained breathing apparatus. Check atmosphere before entering (toxicity and explosion hazard). If atmosphere cannot be checked, do not enter. Let vapours evaporate.</p> <p>Collect spillage in oil drums, metal boxes or salvage packagings. You may use inert absorbent material. Keep collected spillages in well ventilated areas or on deck only.</p>
	Cargo Transport Units (large spillage)	<p>Shut off possible sources of ignition in the space. Provide adequate ventilation. Do not enter deck without self-contained breathing apparatus. Check atmosphere before entering (toxicity and explosion hazard). If atmosphere cannot be checked, do not enter. Let vapours evaporate. Where a ventilation system is used, particular attention should be taken in order to prevent toxic vapours or fumes entering occupied areas of the ship, e.g. living quarters, machinery spaces, working areas.</p> <p>Provide good ventilation of the space. Use water-spray on effluent in the space to avoid ignition of flammable vapours. Wash down to the bottom of the hold. Use copious quantities of water.</p> <p>Treat effluent according to Shipboard Oil Pollution Emergency Plan. Otherwise, radio for expert ADVICE.</p>
Special cases		
UN 1136, UN 1993		These substances may be miscible with water and hence not float on the surface. In this case, SPILLAGE SCHEDULE S – D will be appropriate.
UN 1139, UN 1263, UN 1866		No thorough cleaning of spillage site necessary. Residues will dry out and coat surfaces.