64

REPORTS AND STUDIES

GESAMP

Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships, 2nd Edition

IMO FAO UNESCO IOC WMO UNIDO IAEA UN UNEP UNDP

Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships, 2nd Edition

Published by the
INTERNATIONAL MARITIME ORGANIZATION
4 Albert Embankment, London SE1 7SR
www.imo.org

Printed by Polestar Wheatons (UK) Ltd, Exeter, EX2 8RP

ISSN: 1020-4873

Notes

1. GESAMP is an advisory body consisting of specialized experts nominated by the Sponsoring Agencies (IMO, FAO, UNESCO-IOC, WMO, IAEA, UN, UNEP, UNIDO, UNDP). Its principal task is to provide scientific advice concerning the prevention, reduction and control of the degradation of the marine environment to the Sponsoring Agencies.

2. This report is available in English only from any of the Sponsoring Agencies or online at:

   www.gesamp.org/publications (follow the link for GESAMP Reports and Studies 61-70)

3. GESAMP wishes to draw attention to the fact that the hazard evaluation rationale was conceived for the particular purpose of the development and implementation of the International Convention for the Prevention of Pollution from Ships, MARPOL. The guidance on hazard evaluation contained in this publication is therefore intended primarily to be used for that purpose. Although it should not normally be used out of context, this guidance (or elements thereof) may be found to be useful for other hazard evaluation purposes provided the limitations and restrictions imposed upon such guidance by the hazard assessment rationale, as well as any associated risks, are fully appreciated.

4. While great care has been taken in preparing this publication to ensure the highest possible degree of accuracy, neither GESAMP nor the publishers accept any responsibility for errors or omissions, or for use of the guidance out of the context in which it is presented.

5. Permission may be granted by any one of the Sponsoring Agencies for the report to be wholly or partly reproduced in publications by any individual who is not a staff member of a Sponsoring Agency of GESAMP, or by any organization that is not a sponsor of GESAMP, provided that the source of the extract and the condition mentioned in 3 above are indicated.

6. For bibliographic purposes this document should be cited as:

GESAMP (2014, 2nd ed.). *Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships* (IMO/FAO/UNESCO-IOC/WMO/IAEA/UN/UNEP/UNIDO/UNDP) Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection, Rep. Stud. GESAMP No. 64.

Contact Address:

GESAMP Secretariat
International Maritime Organization
4 Albert Embankment
London SE1 7SR
United Kingdom

Tel + 44 (0)20 7735 3122
Fax + 44 (0)20 7587 3210
Email: GESAMP-EHS@imo.org

GESAMP pages (IMO Website):

http://www.imo.org/ourwork/environment/specialprogrammesandinitiatives/pages/gesamp.aspx

Executive summary

The second edition of the Revised GESAMP Hazard Evaluation Procedure provides an updated set of criteria for evaluating the hazards of chemical substances that may enter the marine environment through operational discharge, accidental spillage, or loss overboard from ships. Hazards to both human health and the marine environment are considered and the information is collated in the form of a "hazard profile", a comprehensive but easily readable fingerprint of the hazard characteristics of each substance. The hazard profiles of substances carried by ships that have been prepared by the Evaluation of the Hazards of Harmful Substances Carried by Ships (EHS) Working Group of GESAMP are published at regular intervals and a "composite list" is available from the International Maritime Organization (IMO) at:

http://www.imo.org/ourwork/environment/pollutionprevention/chemicalpollution/pages/chemicalsreportingforms.aspx

The purpose of the second edition is not to replace the revised GESAMP hazard evaluation procedure, but to update it with as little disruption to the user as possible, only introducing changes where necessary, in particular to ensure harmonization with the United Nations Globally Harmonized System (GHS).

The United Nations Globally Harmonized System of Classification and Labelling (1) was developed to enable the global harmonization of chemical hazard classification and communication in the areas of transport, including the sea, inland waterways, road and rail, as well as consumer, worker and environmental protection. The revised GESAMP hazard evaluation procedure, although specifically developed for the maritime transport of bulk liquid chemicals, is substantially in line with the GHS.

The revised MARPOL Annex II (2) entered into force on 1 January 2007. By this date, the EHS Working Group had converted more than 850 hazard profiles into the new system to allow for the recalculation of the pollution category, ship type and carriage conditions, in accordance with the new requirements. When the first editon of the GESAMP Reports and Studies 64 was published in 2002 (3), it was based on decisions made in the period 1995 to 2000. After more than 10 years from its publication and 15 years from its inception, it was felt by GESAMP that a second edition should be prepared. This edition updates the revised hazard evaluation procedure, in the light of global developments in the understanding of chemical hazards, e.g. the implementation and further amendment of the Globally Harmonized System,

the advent of the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Regulation (4) in Europe and the increasing number of studies available of relevance to maritime transport.

The primary function of the GESAMP EHS Working Group is to evaluate the hazards of bulk liquid substances regulated under MARPOL Annex II and, based on the data received, assign an appropriate pollution category for the substance. On the basis of the GESAMP hazard profile and other properties, the carriage requirements for the substance when carried on a ship are subsequently assigned by IMO.

The system for categorization of noxious liquid substances, as set out in appendix I of MARPOL Annex II, together with ship design and operational requirements, form the regulatory framework for the prevention of pollution from noxious liquid substances from ships. Relevant hazards noted in the GESAMP hazard profile may also be utilized for the classification of substances as a "Marine Pollutant" for packaged goods shipments, in accordance with the requirements set out in the International Maritime Dangerous Goods Code (IMDG Code) (5).

Much has changed since 1972 when, at the request of IMO, GESAMP first introduced principles for evaluating hazards, based on the intrinsic properties of the chemical substance, in support of MARPOL. An important change is one of attitude. The public expects the seas to be kept clean, for the protection of ecosystems, for the provision of healthy, uncontaminated food and for recreational purposes.

Environmental science, including hazard evaluation and risk assessment of chemical substances and mixtures, has evolved considerably over the last 40 years and GESAMP has done much to highlight sources of marine pollution and to assess their relative importance. Knowledge of the effects of chemical substances on human health has also advanced greatly in this time. In both fields, the routes and processes of chemical exposure and subsequent toxic effects are now better understood. Today, standardized testing is able to provide data on a wide range of both human health and environmental criteria used in hazard evaluation and risk assessment.

The volumes of chemical substances and mixtures transported by ship still warrant special measures for the protection of the sea, just as they did when GESAMP first started its work. A single tank on board a bulk chemical tanker may hold up to 3,000 tonnes[1] of a bulk liquid chemical and the ships themselves range from less than 1,000 to well over 60,000 tonnes. GESAMP

[1] Or possibly more, in the case of vegetable oils, which may be carried in larger quantities, subject to the provisions set out in regulation 4.1.3 of MARPOL Annex II.

felt that the ecological and human health risk assessment of chemical substances and mixtures transported by ship would be too complex to address under MARPOL, requiring considerably more environmental data. It was therefore decided, early on in the process, to base the revised GESAMP procedure on an expanded set of hazard end-points.

However, the borderline between hazard and risk is not always clear. The classification system to predict the behaviour of spilled chemicals while based entirely on the intrinsic properties of a chemical, could be seen as a simple form of risk assessment. The aim, however, is to provide an indication of behaviour following a spill and not to provide a quantification of the risks.

The original hazard evaluation rationale was developed by the GESAMP Working Group at the request of IMO (then IMCO), in preparation for the International Conference on Marine Pollution held in 1973. It was approved in 1972 at GESAMP's fourth session as document GESAMP IV/19/ Supp.1 (6).[2] This was superseded in 1982 by GESAMP Reports and Studies No. 17 (7), then by Reports and Studies No. 35 (8) in 1989, and again by the Revised GESAMP Hazard Evaluation Procedure, GESAMP Reports and Studies No. 64 in 2002. The second edition of the Revised GESAMP Hazard Evaluation Procedure, approved by GESAMP at its 40th session in Vienna, 2013, replaces all previous versions.

This second edition retains the revised GESAMP hazard evaluation procedure with all of the main hazard end-points and criteria remaining as they were in the first edition in 2002. GESAMP has sought to introduce further refinement in the interpretation of the long-term human health effects, listed in sub-column D3, to bring it in line with developments in the GHS. In relation to sub-column C3, the application of the GESAMP inhalation toxicity extrapolation method (9), alongside the existing set of measured data, is also described. This was first published in the Report of the 41st meeting of the EHS Working Group (10) and its appearance in the second edition of R and S No. 64 marks the completion of its implementation. It is believed that this is the first time an estimation method has been introduced into the international chemical regulations that substantially replaces the use of animals in acute lethal toxicity testing.

Updated advice on preparing and submitting data to GESAMP, to support the evaluation of substances, is also given. The function of each environmental or human health end-point is separately defined and their criteria described

[2] The report of GESAMP's 4th session held at WHO in Geneva, 1972, refers both to the original meeting document (GESAMP IV/2) and to supplement (GESAMP IV/19 Suppl.), i.e. the hazard evaluation rationale.

in a short introductory section, i.e. the scale on which the end-point is measured, as well as the ranking used, is given under the heading “ratings”. This is followed by a set of supporting principles, given under the heading “implementation”, in order to explain how the scientific data may be applied in hazard evaluation. Finally, updated guidance is given on approved, internationally standardized, experimental and estimation methods for generating the necessary hazard data. Newer methods that avoid the use of animal testing are referenced and their interpretation briefly discussed. The annexes, containing supporting information on testing, have also been updated. Reference is made to the GHS throughout.

The “hazard profile” provides an alphanumerical fingerprint of each substance. The numerical scales start from 0 (negligible hazard), while higher numbers reflect increasing hazard. In this way, information on substances evaluated by GESAMP are made available to the widest possible technical audience in an instantly readable form.

It is hoped that the revised GESAMP hazard evaluation procedure and the scientific work of GESAMP in evaluating chemical substances will continue to play an important role in the protection of the marine environment.

Acknowledgements

Members of the GESAMP EHS Working Group

The second edition of the Revised GESAMP Hazard Evaluation Procedure was prepared by the following members of the GESAMP EHS Working Group:

Tim Bowmer (Ireland), Thomas Höfer (Germany), Derek James (United Kingdom), Stéphane Le Floch (France), Mike Morrissette (USA), Hotaka Saito (Japan), Wenxin Jiang (China), Richard Luit (Netherlands) and Patricio H. Rodriguez (Chile).

IMO

The Working Group wishes to thank the following officers of IMO who supported this work over many years: René Coenen and Edward Kleverlaan (Technical Secretaries of GESAMP) and Norman Soutar (IMO Consultant). Ken McDonald and Patricia Charlebois, Secretaries to the EHS Working Group, are also acknowledged for their contribution.

Contents

Page

Acronyms

ACC	American Chemistry Council
ATE	Acute Toxicity Estimate
BLG	Sub-Committee on Bulk Liquids and Gases[3]
CCC	Sub-Committee on Carriage of Cargoes and Containers (CCC)[4]
CEFIC	European Chemical Industry Council
CG/HCCS	Coordinating Group for the Harmonization of Chemical Classification Systems (IPCS)
CHRIP	Chemical Risk Information Platform (see NITE)
DSC	Sub-Committee on Dangerous Goods, Solid Cargoes and Containers
DWT	Deadweight tonnage is a measure of how much weight a ship is carrying or can safely carry. The term is often used to specify a ship's maximum permissible deadweight, when the ship is fully loaded.
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECHA	European Chemicals Agency
EHS	GESAMP Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships
EPA	United States Environmental Protection Agency
ESPH	Working Group on the Evaluation of Safety and Pollution Hazards of Chemicals and Preparation of Consequential Amendments, a Working Group of the PPR Sub-Committee

[3] BLG Sub-Committee was replaced by the Sub-Committee on Pollution Prevention and Response (PPR) in January 2014.

[4] DSC Sub-Committee was replaced by the Sub-Committee on Carriage of Cargoes and Containers (CCC) in January 2014.

GESAMP	Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection
GHS	Globally Harmonized System of Classification and Labelling of Chemicals of the United Nations
FAO	Food and Agriculture Organization of the United Nations
HPV	High Production Volume (Chemicals Programme)
IAEA	International Atomic Energy Agency of the United Nations
IBC Code	International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (IMO)
IGC Code	International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IMO)
ILO	International Labour Organization of the United Nations
IMCO	Inter-Governmental Maritime Consultative Organization (predecessor of IMO)
IMDG Code	International Maritime Dangerous Goods Code
IMO	International Maritime Organization of the United Nations
IMSBC Code	International Maritime Solid Bulk Cargoes Code
IOMC	Inter-Organization Programme for the Sound Management of Chemicals (sponsored by six UN agencies and the OECD)
IPCS	International Programme on Chemical Safety (sponsored by three UN agencies)
ISO	International Organization for Standardization
JCIA	Japan Chemical Industry Association
MARPOL	International Convention for the Prevention of Pollution from Ships
MEPC	Marine Environment Protection Committee of the IMO
NITE	Japanese National Institute of Technology and Evaluation
NOEC	No Observed Effect Concentration
OECD	Organisation for Economic Co-operation and Development
PCB	Polychlorinated biphenyl

PCDD	Polychlorinated Dibenzodioxin
PPR	Sub-Committee on Pollution Prevention and Response
QSAR	Quantitative Structure Activity Relationship
REACH	European regulation concerning Registration, Evaluation, Authorisation and Restriction of Chemicals
Sida	Swedish International and Development Cooperation Agency
UN	United Nations
UNCED	United Nations Conference on Environment and Development
UNCTDG-GHS	United Nations Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals
UNDP	United Nations Development Programme
UNEP	United Nations Environment Programme
UNESCO-IOC	United Nations Education, Scientific and Cultural Organization – International Oceanographic Commission
UNIDO	United Nations Industrial Development Organization
US EPA OPPTS	United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances
WMO	World Meteorological Organization of the United Nations

1 – Introduction

1.1 GESAMP

GESAMP was established in 1969 as an expert group to advise its sponsoring organizations on issues related to marine pollution. Its mandate was widened in the 1990s to address marine environmental protection. It is supervised by an Executive Committee, consisting of its Chairman, Administrative Secretary (IMO) and Technical Secretaries representing its nine UN sponsoring agencies. It is an interagency scientific advice body of the UN system, responding to requests for advice from its sponsoring agencies. Following an external review in 2003, a renewed and revitalized GESAMP reconvened in Paris in 2006 with financial support from the Swedish International Development and Cooperation Agency and two new UN agency sponsors, UNIDO and UNDP. It currently has working groups (WGs) and task teams addressing a wide range of topics related to the protection of the marine environment, as follows:

WG 1 Evaluation of the Hazards of Harmful Substances Carried by Ships (IMO)

WG 34 Review of applications for "Active Substances" to be used in ballast water management systems (IMO)

WG 37 Metals in the marine environment (UNEP)

WG 38 The atmospheric input of chemicals in the oceans (WMO)

WG 39 Global trends in pollution of coastal ecosystems: retrospective ecosystem assessment (IAEA)

WG 40 Sources, fate and effects of micro-plastics in the marine environment – a global assessment (UNESCO-IOC)

The Task Team on the Trans-boundary Waters Assessment Project (Open Ocean Pollution)

The progress of the working groups is reviewed annually by GESAMP. They are led by GESAMP members and populated by specialists chosen from around the world, acting in their personal capacity as independent scientific experts.

GESAMP publishes its findings through its sponsoring agencies as Reports and Studies, of which 87 issues have appeared to date. Full information on GESAMP can be found at: www.gesamp.org.

1.2 Marine pollution from ships: historical background

The MARPOL Convention is the main international convention covering prevention of pollution of the marine environment by ships from operational or accidental causes. It is a combination of two treaties adopted in 1973 and 1978 respectively and updated by amendments through the years. It includes six annexes regulating the prevention and control of marine pollution from ships through:

Annex I	oil
Annex II	noxious liquid substances in bulk
Annex III	harmful substances carried by sea in packaged form
Annex IV	sewage from ships
Annex V	garbage from ships
Annex VI	air pollution from ships

Prior to 1973, IMO in categorizing the hazards of chemical substances carried by ships, experienced difficulties for the development of suitable control measures. It therefore requested GESAMP to consider the hazards that such substances might pose when deliberately or accidentally discharged into the marine environment. The following potential effects were to be taken into account:

- damage to living resources;
- hazards to human health;
- reduction of amenities; and
- interference with other uses of the sea.

In the light of this request from IMO for external assistance, in 1971, GESAMP agreed that an ad hoc panel of IMO and GESAMP experts should be established to develop methods for assessing the hazards of chemical substances transported by ships. The ad hoc panel met prior to the International Conference on Marine Pollution and its outcome was incorporated into MARPOL.

Following the adoption of MARPOL, GESAMP was requested to continue the task of evaluating the hazards of substances proposed for carriage by ships. In 1974, it established the EHS Working Group, which has met on an annual basis since that time. The terms of reference for the EHS Working Group are included in annex I, while the list of past and current members is given in annex II.

Harmful substances carried by ships are defined under MARPOL, article 2(2), as:

> *"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".*

GESAMP was requested to evaluate the properties of substances transported in bulk by sea in accordance with MARPOL Annex II. Substances carried as packaged dangerous goods are defined under MARPOL Annex III [2] as *"those substances which are identified as Marine Pollutants in the IMDG Code"*.

Shippers of dangerous goods in packaged form are required to self classify substances based on the criteria set out in the IMDG Code for classification as a "Marine Pollutant". The CCC Sub-Committee (formerly the DSC Sub-Committee) of IMO is responsible for the official listing of cargoes in the IMDG Code. Accordingly, the EHS Working Group does not evaluate chemicals transported as packaged goods. However, where needed, the GESAMP hazard profiles are available to support self-classification by shippers.

1.3 Development of the revised GESAMP hazard evaluation procedure

By the mid 1990s, IMO's MEPC had begun to review MARPOL Annex II, which regulates the control of pollution by "noxious liquid substances" carried in bulk by ships. The intention was to simplify the text, while at the same time taking into account any new developments since its adoption.

International, non-governmental organizations, as well as government Administrations, requested that, as part of the hazard evaluation procedure developed by GESAMP more than 20 years previously, additional end-points be considered, such as physical characteristics, some measure of persistence or biodegradation and chronic aquatic toxicity. The EHS Working Group members, as experts in various aspects of the hazard evaluation of chemicals, were also of the opinion that the system was in need of review, in order to take account of advances in environmental sciences in the intervening years. In response, MEPC established a panel of experts in 1995 to review the GESAMP evaluation procedure. This expert panel made a number of recommendations, which were endorsed in principle by GESAMP at its 26th session (March 1996). Taking these views into account, the EHS Working Group commenced the task of revising the GESAMP hazard evaluation procedure.

1.4 Global harmonization of chemical classification systems

In 1992, the United Nations Conference on Environment and Development (UNCED) (11), through its Agenda 21,[5] Chapter 19, entitled "Environmentally Sound Management of Toxic Chemicals, Including Prevention of Illegal International Traffic in Toxic and Dangerous Products", established a programme on the "harmonization of classification and labelling of chemicals".

Its objective was to ensure that:

> *"a globally harmonized hazard classification and compatible labelling system (GHS) including material safety data sheets and easily understandable symbols, should be available, if feasible, by the year 2000".*

UNCED identified the International Programme on Chemical Safety (IPCS) as the nucleus for international cooperation on Chapter 19 activities. Following the establishment of the InterOrganization Programme for the Sound Management of Chemicals (IOMC) in 1995, the Coordinating Group for the Harmonization of Chemical Classification Systems (CG/HCCS), which had already been established by ILO under the auspices of IPCS, was renamed the IOMC CG/HCCS and was given the task of promoting and overseeing the work of developing the GHS. The CG/HCCS had requested the Organisation for Economic Co-operation and Development (OECD) to act as the focal point for development of classification systems for all human health and environmental hazards. For this purpose, OECD established its Advisory Group on Harmonization of Classification and Labelling in 1994 to oversee and manage this work. These activities resulted in the establishment of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), which was to be implemented by a new (GHS) Sub-Committee of the UN Committee of Experts on the Transport of Dangerous Goods. During the development of the GHS, concerns arose regarding the way in which a "harmonized" classification system might be used and whether it would meet the needs of its various end users. In this regard, attention is drawn to the following principle of the GHS:

> *"harmonization means establishing a common and coherent basis for chemical hazard classification and communication, from which the appropriate elements relevant to means of transport, consumer, worker and environment protection can be selected".*

[5] Agenda 21 is a non-binding voluntarily implemented action plan of the United Nations with regard to sustainable development resulting from the UN Conference on Environment and Development (UNCED) held in Rio de Janeiro, Brazil, 1992.

It was also considered essential that uniform cut-off values for each hazard end-point be identified as part of the evaluation criteria, thus forming a fundamental basis for the GHS.

The activities of the OECD in developing the GHS, and those of GESAMP in developing its revised Hazard Evaluation Procedure, ran concurrently between 1995 and 1998. Representatives of IMO, as well as GESAMP experts, participated in meetings of the OECD Advisory Group on Harmonization of Classification and Labelling and, in particular, its ad hoc Working Group on the Classification of Substances Dangerous to the Aquatic Environment.

Accordingly, the revised GESAMP Hazard Evaluation Procedure was developed based on these principles of harmonization, while bearing in mind the specific needs of evaluating chemical substances for transport by ship.

Any amendments made during the implementation of the GHS were closely monitored, as any change in the criteria or the cut-off values could potentially impact the existing hazard profiles or their classification under existing maritime regulations. In particular, amendments to the GHS may have necessitated an amendment to MARPOL and a revision of the GESAMP Hazard Evaluation Procedure, including potential reclassification of products. Some amendments to the GHS were introduced in 1st, 2nd, 3rd and 4th revised editions, published by the United Nations. However, due to the aforementioned limitations, not all of these could be transcribed directly into the GESAMP Hazard Evaluation Procedure. The second edition of the GESAMP Hazard Evaluation Procedure has therefore taken into consideration the consolidated amendments to the 4th edition of the GHS.

1.5 The shipping industry and the transport of bulk liquid substances

The revised GESAMP Hazard Evaluation Procedure is used by the GESAMP EHS Working Group for the evaluation of the hazards of chemical substances and mixtures in liquid form, as governed by MARPOL Annex II and the IBC Code. Substances not covered by the Procedure are provided below, together with the respective regulatory instruments governing their carriage:

- packaged dangerous goods (IMDG Code)
- solids carried in bulk (IMSBC Code) (12)
- gases carried in bulk (IGC Code) (13)
- mineral oils carried in bulk (MARPOL Annex I)
- radioactive substances (in respect to their radiation hazard).

These are the subjects of different scientific expertise and regulatory controls outside of the remit of the GESAMP EHS.

1.5.1 *Bulk liquid cargoes*

A modern chemical tanker may range in size from 1000 to over 60,000 tonnes dead weight tonnage (DWT) and, for the purpose of carrying noxious liquid substances in bulk, many of these will be of double hull construction to prevent the release of cargo in the event of collision or grounding. Tankers carrying less hazardous chemical substances may be of less sophisticated construction, and may be single hulled. However, based on current regulations, most new chemical tankers will be of double hulled construction. A large chemical tanker may be equipped with as many as 50 separate tanks. Each tank can be filled and emptied independently via its cargo pumps and associated piping connected to a manifold, usually located amidship on deck. Some vessels may also carry additional cylindrical tanks attached to the deck, often giving the chemical tanker its characteristic profile.

At each port of call, the chemical tanker will generally load and unload several tanks at one or more chemical terminals within the harbour. This requires that the empty tanks are cleaned and that the residues are removed while in port, ready for receipt of the next cargo. There is a complex protocol for determining which cargoes may be suitably loaded in a particular tank. This depends on the tank material/lining, the adjacent cargoes (depending on their safety compatibility), and previous cargoes (to avoid contamination).

Chemical tankers are required to discharge tank washings and the designated pollution category under MARPOL Annex II will determine what the vessel operator must do with these residues. It is important for the protection of the marine environment that tanks are first stripped of their bulk liquid cargo to the maximum extent. This is also clearly in the economic interest of the owners of both the ship and its cargo. It is generally accepted that modern chemical tankers can strip their tanks of non-viscous liquid cargo to 75 litres or less. The double hull allows room for a small well in which the “cargo line” is placed so that only the cargo in the bottom of the pumping well remains after the tank has been emptied. Tanks containing cargoes deemed to be particularly hazardous to the marine environment or those with a high viscosity, generally require a prewash (e.g. a hot water wash with tank cleaning additives) after emptying, in order to remove any clinging material. These residues are then discharged to shore. Some viscous substances are pumped on and off tankers at elevated temperatures and, for such cases, a prewash is not always mandatory.

While reception facilities are available at many major ports and harbours, they are absent in many parts of the world. It is also unlikely that the technology

and facilities for dealing effectively with hazardous waste is available in every country. In the absence of port reception facilities, the tank washings from particularly hazardous cargoes may have to be transported onwards to another port where such facilities are available. The residues of hazardous substances that do not require a prewash are permitted to be discharged into the sea, but only in limited quantities as follows:

- under the waterline
- 12 miles offshore
- with 25 metres or more of water under the keel
- at a speed of not less than 7 knots.

New MARPOL regulations for chemical tankers came into effect on 1 January 2007, including:

- revised "ship typing", i.e. the design of ships required for cargoes of various hazards (e.g. double hull);
- revised guidelines for the categorization of noxious liquid substances (assigned on the basis of the GESAMP hazard profile);
- revised carriage conditions, i.e. the minimum criteria required for safe handling and transport of each substance on board;
- revised discharge criteria applied for cargo, with a view to limiting operational discharges taking into account advancing technologies.

New chemical tankers have tank stripping equipment that can reduce the volumes of cargo residue and, therefore, the volume of operational discharges at sea, or to port reception facilities, to a very low level.

1.5.2 *Cleaning additives*

Aside from bulk liquid cargoes, GESAMP hazard profiles have an important role in the evaluation of cleaning additives, which may be used in tank washing operations to remove cargo residues. In accordance with regulation 13 of MARPOL Annex II, which sets out the provisions for the "control of discharges of residues of noxious liquid substances", restrictions are placed on the cleaning additives permitted for use as follows:

> *"13.5.2 When small amounts of cleaning additives (detergent products) are added to water in order to facilitate tank washing, no additives containing Pollution Category X components shall be*

used except those components that are readily biodegradable and present in a total concentration of less than 10% of the cleaning additive. No restrictions additional to those applicable to the tank due to the previous cargo shall apply."

To determine whether a cleaning additive component complies with the provisions of 13.5.2, information for sub-columns A1, A2, B1 and D3 of the GESAMP Hazard Profile is required, together with the component's usage level.

On this basis, for cleaning additive components, it is possible to request a short GESAMP hazard profile, comprising only these four sub-columns, so that the information required in the 'Revised tank cleaning additives guidance note and reporting form' (MEPC.1/Circ.590), may be provided to IMO (14).

It should be noted that such a profile is suitable only for the purposes of assessing components of cleaning additives used solely for tank cleaning operations and not intended for transport. If these products are intended for transport, then the full range of required information must be provided. In the GESAMP Composite List, profiles for cleaning additives and their components are clearly marked accordingly to indicate their status.

1.5.3 *Mixture components*

Similar to the short hazard profiles assigned to components of cleaning additives, a restricted profile may also be given for components used only in mixtures, i.e. where the component is not intended to be shipped in its pure form. In this case, information must be provided for sub-columns (A1, A2, B1 and D3), as is the case for cleaning additive components, as well as for sub-columns B2 and E2. A short GESAMP hazard profile may then be provided, comprising just these six sub-columns, in accordance with the information required in Revised Guidelines for the Provisional Assessment of Liquid Substances Transported in Bulk (MEPC.1/Circ.512) (15).

In this instance, it should be noted that such a profile is suitable only for mixture calculation purposes and that such materials cannot be shipped in pure form in bulk, without further information being provided. In the GESAMP Composite List, such profiles are marked accordingly to indicate their status.

2 – The GESAMP Hazard Profile under the revised procedure

2.1 Aims of the revision

In revising its hazard evaluation procedure, GESAMP made every effort to address the following needs:

- to provide a comprehensive and practical procedure based on current knowledge of environmental science and occupational health;
- to provide a set of human health and safety criteria to assist in the assignment of the "carriage requirements" for each substance, in accordance with the IBC Code, in particular, for the protection of the crew on board chemical tankers;
- to help protect the marine environment from the effects of operational discharges, accidental spillage of substances from ships;
- to include hazard end-points that would assist IMO to regulate the transport of bulk chemical cargoes; and,
- enhance harmonization with the GHS.

2.2 Structure of the revised GESAMP Hazard Profile

During the 1995 to 1998 review process, the familiar five-column system was retained; however, each column was divided into several sub-columns, in order to further define the underlying hazard information, as far as possible, and make it clearer to the end user. A summary of the end-points used can be found in Table 1.

The revised GESAMP hazard profile consists of the end-points listed in Table 1. Each of the 13 sub-columns represents an environmental or human health end-point or "effect" category, although there may still be several underlying elements, e.g. toxicity to fish, crustaceans and microalgae in Sub-column B1 (acute aquatic toxicity).

A summary of the GESAMP hazard profile and its ratings can be found on the inside back cover.

Table 1 – *Summary of the end-points used in the revised GESAMP hazard evaluation procedure*

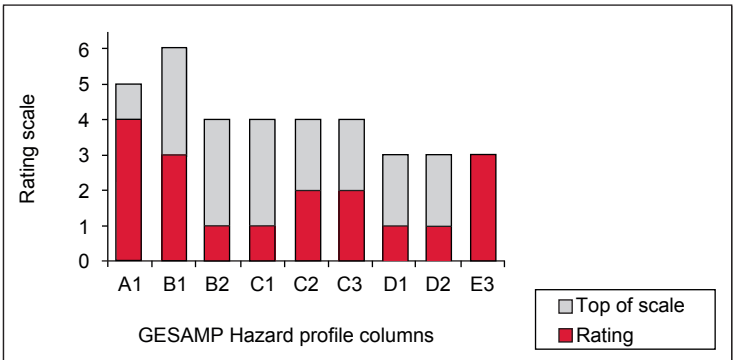
Title	Sub-column	Hazard criterion	Comment
A Bioaccumulation and Biodegradation			
	A1	• Octanol/Water partition coefficient (log Pow) and/or Bioconcentration factor (BCF)	• Measures of the tendency of a substance to bioaccumulate in aquatic organisms
	A2	• Ready biodegradability	• Used to identify substances with biodegradation characteristics
B Aquatic toxicity			
	B1	• Acute aquatic toxicity	• Toxicity to fish, crustaceans and microalgae, generally measured in appropriate laboratory tests
	B2	• Chronic aquatic toxicity	• Reliable data on chronic aquatic toxicity, based on fish, crustaceans and microalgae
C Acute mammalian toxicity			
		Distinguishes lethal toxicity as a result of exposure through the following routes:	Measured in appropriate tests with laboratory animals, based on human experience or on other reliable evidence
	C1	• Oral	
	C2	• Dermal	
	C3	• Inhalation	
D Irritation, corrosion and long-term mammalian health effects			
		Distinguishes toxicity as a result of the following:	Measured in appropriate tests with laboratory animals, based on human experience or on other reliable evidence
	D1	• Skin irritation and corrosion	
	D2	• Eye irritation and corrosion	
	D3	• Long-term health effects	Carcinogenicity, Mutagenicity, Reprotoxicity, Sensitization, Aspiration, Specific Target Organ Toxicity (including Neurotoxicity and Immunotoxicity)
E Interference with other uses of the sea			
	E1	• Tainting[6]	• Off-flavours in seafood following spillage of cargo
	E2	• Behaviour of chemicals in the marine environment and physical effects on wildlife and on benthic habitats	• Behaviour in seawater, i.e. the tendency to form slicks or blanket the seabed, evaluated on the basis of solubility, melting point, vapour pressure, specific gravity and viscosity
	E3	• Interference with coastal amenities	• Potential need for closing beaches due to physical hazards and specific health concerns

[6] Note: This hazard criterion is no longer required.

A hazard profile is illustrated below in Figure 1, where it can be seen that the substance in question:

- has a high potential to bioaccumulate in aquatic organisms (A1);
- is not readily biodegradable (A2);
- has a moderate acute and a low chronic aquatic toxicity (B1 and B2);
- has a low oral, moderate dermal and a moderate inhalation toxicity to mammals (C1 to C3);
- is mildly irritating to skin and eye (D1 and D2);
- is potentially carcinogenic (D3);
- is not liable to taint seafood (E1);
- is a floating substance liable to form persistent slicks on the water surface (E2); and
- has a significant impact to onshore and offshore amenities (E3).

Figure 1 – *Graphical and tabular illustration of a revised GESAMP hazard profile for a given substance*



A1	A2	B1	B2	C1	C2	C3	D1	D2	D3	E1	E2	E3
4	NR	3	1	1	2	2	1	1	C	0	Fp	3

The explanation of the descriptive terms and the largely quantitative ratings is developed in detail in section 4. The rating scales begin at 0 ("practically non-hazardous" or of "negligible hazard") and run to a maximum of 3 to 6, indicating an increasingly severe hazard.

2.3 Other uses of the profile

The GESAMP hazard evaluation procedure was designed to assist with the implementation of MARPOL. However, it also provides a range of information on the properties of substances, with respect to the protection of the aquatic environment and human health, which may be suitable for other uses, such as:

1. In an emergency context to help to determine the potential ecotoxicological and physical hazards of the product released, where:

- columns A and B may help to perform an environmental impact assessment of the incident on a short or long-term basis;
- ratings in columns C and D (Human Health) can provide operational personnel with information that can be used for taking appropriate safety precautions when responding to accidental spills (e.g. selection of protective clothing and respiratory equipment); and
- column E may help the appointed authorities during maritime emergencies in the choice of the response option which can be employed. A floating spilled product could be recovered from the water surface, while a dissolving product in the water column or an evaporating product in the atmospheric compartment may need to be monitored. Some substances could create hazards on the coastline and measures to restrict access may need to be considered (e.g. evacuation of areas such as beaches, a ban on fishing or swimming, etc.).

As the cut-off criteria in columns A, B, C[7] and D are harmonized with the respective building blocks of the GHS, the GESAMP Composite List which currently contains over 950 hazard profiles can therefore be used (with some limitations) as an indicative list of classifications according to the GHS, based on data available in the GESAMP files.

2. The hazard profiles may also have some use in assessing discharges of effluents into the aquatic environment on a continuous-release basis, such as from sea-based activities (e.g. offshore platforms) or from land-based activities.

[7] For column C3, some restrictions apply concerning the classification of mists and aerosols under the GHS.

3 – Preparation of data – Advice to manufacturers and Administrations

In accordance with MARPOL Annex II, bulk liquid substances are generally those which can be pumped into fixed tanks on board ships. They include pure substances and mixtures; however, mineral oils are excluded, as they are regulated under Annex I of MARPOL and are carried in oil tankers. Some bulk liquids are solid at ambient winter and summer sea temperatures and the tanks are therefore heated to prevent solidification and possible expansion, and to ensure that they can be pumped on board and off. Bulk liquids also include a range of mineral materials carried as aqueous slurries, e.g. calcium carbonate and coal slurry. Some food grade substances, such as orange juice and concentrates, require refrigeration. Vegetable oils, one of the highest volume groups of substances transported, also fall under the umbrella of bulk liquid substances and are regulated as chemicals under MARPOL Annex II. Some mixtures of chemicals are regularly carried in mineral oil and, although mineral oils in general are carried under Annex I of MARPOL, some Annex II substances do indeed consist of hydrocarbon distillates, such as steam cracked naphtha and pyrolysis gasoline. The range of chemistries, physico-chemical properties and environmental behaviour encountered is vast, as are the related potential hazards to the marine environment and human health. The following sections (3.1 to 3.11) provide information on data quality, confidentiality, how to deal with missing data, read across, weight of evidence, as well as initial guidance on dealing with mixtures.

3.1 Submitting data to GESAMP

Submissions on chemical substances proposed for transport by ship that require evaluation by GESAMP, should be addressed to:

The Secretary of the GESAMP EHS Working Group
Marine Environment Division
International Maritime Organization
4 Albert Embankment
London SE1 7SR
United Kingdom
Email: GESAMP-EHS@imo.org

Copies of the GESAMP-EHS Product Data Reporting Form, reproduced in annex VI of this document, may be obtained from IMO or, along with other related documents, may be accessed directly at:

http://www.imo.org/ourwork/environment/pollutionprevention/chemicalpollution/pages/chemicalsreportingforms.aspx

Many of the chemical substances and mixtures proposed for carriage by ship are identified under trade names by the submitting organization. To allow clear identification, GESAMP and IMO may assign a chemical name and/or a product name to the substance. The appropriate naming of substances is considered further in annex III. GESAMP requires detailed information on the exact composition of a chemical substance and mixtures. If the composition of a substance that has already been evaluated is altered, it is the responsibility of the manufacturer to inform GESAMP and IMO, accordingly.

The GESAMP EHS Working Group generally meets once each year to consider requests to evaluate new chemical substances, to address correspondence with the chemicals industry or to otherwise amend existing hazard profiles based on new information. Entities planning to submit data on chemical substances for evaluation by the GESAMP EHS Working Group are advised to find out the dates of the relevant meeting through the contact point listed above. Having submitted data, it is often helpful to have a representative of the company available by telephone or email during EHS meetings, in case contact is required to clear up any issues relating to the evaluation of their chemical substances.

3.2 Evaluation charges

Following a decision taken by the Marine Environment Protection Committee, a standard charge for the evaluation of all substances and the assignment of a GESAMP hazard profile has been introduced. This applies regardless of whether a full hazard profile or a short profile (as for cleaning additive or mixture components) is requested and details of current charges are contained in the IMO circular BLG.1/Circ.28,[8] "The Introduction of Charges for Product Evaluation Undertaken by GESAMP/EHS".

GESAMP, through its EHS Working Group, encourages industry involvement in the preparation of the hazard profiles. The sessions of the GESAMP EHS Working Group are closed in order to preserve the confidentiality of proprietary trade information. However, representatives from chemical manufacturers, their trade associations or sector groups, as well as shipping agencies, are frequently invited to provide statements or to comment on specific items under discussion. Such contributions are particularly welcomed by GESAMP.

The results of the evaluation of chemical substances are published in the meeting reports of the GESAMP EHS Working Group. Following a decision

[8] Available to IMO Member States at IMODOCS or by contacting the GESAMP EHS Secretariat.

by GESAMP at its 32nd Session[9] (16) and in order to avoid any delay in the process of hazard evaluation and pollution categorization, the EHS Working Group notifies IMO directly of any new or revised hazard profiles, without prior approval from GESAMP. This decision was reviewed and endorsed by GESAMP at its 40th meeting in Vienna, in 2013.

An updated list of hazard profiles, together with the report of the latest GESAMP EHS Working Group meeting, is published annually by IMO in the form of an IMO PPR.1/Circular and distributed to IMO Member States and observer organizations. The latest GESAMP Composite List can be accessed on the IMO website under the heading 'Related documents' at:

http://www.imo.org/ourwork/environment/pollutionprevention/chemicalpollution/pages/chemicalsreportingforms.aspx

3.3 Data recording by the EHS Working Group

In addition to retaining hard copies of the supporting data on each substance, the EHS Working Group records the rationale behind its ratings for each hazard end-point (sub-column) of the hazard profile. With careful recording of all decisions on ratings, the EHS Working Group is able to respond to any queries from manufacturers and Administrations with regard to its decisions. The rationale, as well as the supporting data, are added to the files for each substance which are maintained by IMO, on behalf of the EHS Working Group.

3.4 Data confidentiality

Nearly 1,000 substances, including many mixtures, have been re-evaluated by the EHS Working Group in the last 15 years. Original data submitted by manufacturers on these substances are stored securely at IMO and remain confidential. Such proprietary data are only made available to members of the GESAMP EHS Working Group for the purposes of establishing or reviewing a hazard profile.

---

[9] GESAMP, at its 32nd meeting, decided the following, in relation to its EHS working group:

> *"6.11 ……it was agreed that this independence could only be maintained by the Group [EHS] being under the auspices of GESAMP which would continue to provide guidance regarding the membership of the Group, defining its method of work and reviewing the processes involved, such as the content of Reports and Studies 64.*
>
> *6.12 In order to expedite the use of the Hazard Ratings by IMO, it was proposed that the hazard evaluations, developed by the Group, could be reported directly to IMO bodies at the same time as GESAMP."*

3.5 Sources of data

In recent years, a large volume of new environmental data on industrial chemicals has entered the public domain from the following sources:

1. American Chemistry Council (ACC), European Chemical Industry Council (CEFIC) and Japan Chemical Industry Association (JCIA) were active within the voluntary High Production Volume (HPV) Chemicals Programme, which ended in 2013. Data are contained in Substance Information Data Sheets (SIDS) published by OECD (17).

2. European Chemical Agency's (ECHA) (18) on-line databases contain summaries of data on thousands of chemicals registered in Europe under the REACH Regulation.

3. United States Environmental Protection Agency (EPA) provides a wide range of databases on chemical safety, including human health and the environment (19).

4. Japanese National Institute of Technology and Evaluation's (NITE), Chemical Risk Information Platform (CHRIP) (20) provides hazard information. Much of the physico-chemical, acute and chronic ecotoxicology, biodegradation and bioaccumulation hazard data is original and generated by government-sponsored programmes in Japan.

These are the primary sources of data on chemical hazards.

3.6 Data quality

While all relevant, high-quality data are acceptable for review in support of hazard profiles, GESAMP has a strong preference for experimental data generated in compliance with the OECD Principles of Good Laboratory Practice (21). The EHS Working Group searches for qualifying information, to complement and confirm the scientific data submitted by manufacturers. Where environmental data are concerned, the log Pow is generally calculated from the molecular structure (where known) of all organic chemicals and used as a quality control measure for both bioconcentration and aquatic toxicity data. The accuracy of data contained in submissions is also cross-checked against information available in the open literature. Expert judgement is used by the EHS Working Group to evaluate the quality and interpret the results of older, often non-standard studies.

3.7 Missing data

GESAMP strives to issue the hazard profiles in the most complete form possible, i.e. with ratings in all of the columns appropriate for the purpose intended (i.e. carriage as a bulk liquid substance, as a component in a mixture or as a cleaning additive). This, however, depends on the suitability and reliability of the data submitted by the manufacturer or shipper of the substance. Care should be taken to provide full supporting references and copies of the appropriate test laboratory reports in support of each submission. Submissions that are missing essential information may be rejected, pending receipt of more complete data.

When reviewing the profiles of problematic substances, e.g. where data may be lacking, the EHS Secretariat may invite the chemical industry to cooperate in providing additional data. Such substances are then reviewed again, once sufficient data has become available.

In the context of bulk liquid transport by ships, it should be noted that while several of the sub-columns are not used for assigning pollution categories or for defining the tank protection standards for transport ("ship typing"), they may be needed to assign carriage requirements, based on safety considerations.

3.8 Estimation techniques

Where experimental data on bioaccumulation, biodegradation, or acute aquatic toxicity are not available, then generally accepted estimation techniques may be applied, on a case by case basis. Only reliable and validated Quantitative Structure Activity Relationships (QSARs) for estimating the acute aquatic toxicity of the chemical group in question are acceptable. The OECD principles for validating QSARs (22) should be followed by the manufacturer and a suitable justification provided for the submitted data.

In the absence of measured data, estimates generated by the US EPA's KOWWIN model, which estimates the log octanol-water partition coefficient of chemicals using an atom/fragment contribution method, may be acceptable. Estimation techniques for biodegradation, such as the set of six US EPA models known as BIOWIN, may also be acceptable to show that a substance is not readily biodegradable, in order to avoid further testing. Both of the above models are contained in the US EPA's Estimation Program Interface (EPI) Suite™ (23).

The EHS acute inhalation toxicity estimation rationale, outlined in section 4.3.4, is used to fill in missing data. Estimations for other acute end-points may also be acceptable, provided that adequate justification is included with the submitted data.

Extrapolation techniques for deriving mammalian data on long-term toxic and chronic aquatic toxicity are generally regarded as being inadequate. However, this is an aspect that is kept under review by the EHS Working Group.

3.9 Rating by read across

In cases where data on a structurally similar substance(s) is available, this may be used as a basis to provide a rating for one or more hazard end-points (sub-columns), whether related to the marine environment or to human health.

In such cases, convincing evidence of the structural similarity, physico-chemical properties, common molecular functional groups, metabolites, mechanism of action or other such characteristics of the analogous substance(s) should be provided to the EHS Working Group of GESAMP. Where manufacturers choose to submit data on a closely analogous substance, then the exact relationship and complete supporting information should be provided. Significant gaps in the available data on the supporting substance may lead to rejection. In such cases, estimated (non-experimental) data may be considered.

In the case of a substance belonging to a homologous series, manufacturers are encouraged to provide a comprehensive data set for the selected homologues and to clearly justify the arguments for read across of the selected hazard end-points to the target substance.

It should be borne in mind that read across needs to be approached on the basis of individual hazard criteria (end-points) and that it may not be possible to read-across data for some end-points, even where chemical structures are quite similar.

It is always advisable to contact the GESAMP-EHS Secretariat prior to making a submission on the basis of read across.

3.10 Rating of mixtures

Extensive consideration has been given to the classification of mixtures as part of the GHS. This is based on a separate consideration of each hazard end-point. The GHS defines "substances" as being:

> *"chemical elements and their compounds in the natural state or obtained by any production process, including any additive necessary to preserve the stability of the product and any impurities deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition".*

A "mixture" is defined as:

> *"mixtures or solutions composed of two or more substances in which they do not react".*

The EHS Working Group has considered many mixtures, including natural mixtures, such as hydrocarbon distillates, and other prepared mixtures, such as solutions, preparations, etc.

Whilst in general, the mixture classification rules, as outlined in the GHS, could be applied, it may be appropriate to test some more complex mixtures in their entirety for some end-points. As many products evaluated by the EHS Working Group represent bulk cargo entries in the IBC Code which can vary in their composition, e.g. when produced at different locations, some of the GHS mixture rules cannot be directly applied. The reader is therefore referred to the rules for mixtures, as outlined in MARPOL Annex II and the IBC Code (24).

Annex III of this report contains guidance on the naming of substances, particularly mixtures, for submission to the GESAMP EHS Working Group. The hazard profile provides an ideal format for a modular approach to mixtures, allowing components to be compared at a glance.

At present, the EHS Working Group rates the hazard of mixtures on a case by case basis, often focusing on the most hazardous components present in significant quantities. The rationale behind each decision is recorded in the substance file retained by IMO. It is recognized that where the aquatic environment is concerned, data on bioconcentration and biodegradation may need to be generated separately for the significant components of a mixture, rather than for the mixture as a whole.

3.11 Weight of evidence

For the human health criteria contained in the hazard profile, the EHS Working Group prefers the use of appropriate experimental data. However, human experience, based on instances of accidental poisoning or from epidemiological studies, is also taken into account. All available information is considered by the experts and ratings are given on the basis of the total weight of evidence, for the hazard evaluation of substances.

Where acute aquatic toxicity is concerned and only a single set of data is available, e.g. an acute fish, crustacean and algal toxicity tests, then the lowest LC_{50} value of the three is used to provide a rating. However, many substances have acquired large databases for many of the hazard end-points in recent years and a weight of evidence approach has become necessary to ensure that the rating reflects the body of data, rather than simply the most conservative value.

The distribution of data for a given end-point often lies across more than one rating band. In such cases, the EHS Working Group will examine the data at the upper and lower ends of the distribution to assess whether to include them or to disregard such data as outliers. More severe, but less reliable data may also be rejected in favour of more reliable test results. Where the aquatic environment is concerned, taxonomic considerations, such as whether the organism is of marine or freshwater origin, may also be taken into account.

3.12 Rating notation and confidence in the supporting data

The GESAMP EHS Working Group assigns a rating in one of the following ways:

- a full rating, indicating consensus based on a review of data specific to a product, or on adequate supporting evidence;
- a rating "in brackets" indicates when an end-point has been rated by read across to a similar substance, or by an acceptable estimation method. A rating in brackets indicates sufficient confidence to provide a rating. It should be pointed out that such ratings are utilized by IMO in defining the pollution category, ship type and carriage requirements; and
- the symbol "NI" (no information) is placed in any sub-column of the hazard profile to indicate that insufficient data were available to allow a rating for that end-point. In such circumstances, it may not be possible to categorize the product under MARPOL Annex II.

The GESAMP EHS Working Group makes every effort to list the hazards to human health including the long-term health effects covered in sub-column D3. This is based on the evidence available at the time the substance is reviewed. Accordingly, one or more of the set of notations defined in section 4.4.3 is placed in sub-column D3. However, this process is not exhaustive and the absence of any or all notations should not be taken to mean that such hazards do not exist.

3.13 Review of substances by the GESAMP EHS Working Group

The revised GESAMP hazard profiles are subject to regular review, either at the request of manufacturers, or by the EHS Working Group itself, which checks individual substances and occasionally whole groups of chemically related substances, adding new information and updating the profiles, accordingly. These amended profiles are used for assigning carriage conditions, including the pollution category for substances and mixtures according to MARPOL Annex II and the IBC Code respectively, although changes may take some time to implement.

4 – Hazard evaluation end-points

This section describes the hazards arising from the intrinsic properties of chemical substances and how they are evaluated. The hazard end-points are set out below in the order of the GESAMP hazard profile columns.

The following sections are provided with individual introductions to each hazard end-point. This is followed by a description of the ratings and the manner in which they are applied. Each section contains guidance on selecting the appropriate test methods (see Boxes 1 to 10).

4.1 Column A: Bioaccumulation and Biodegradation

The tendency for substances to bioaccumulate and biodegrade is reflected in two sub-columns under column A of the hazard profile:

- A1: Bioaccumulation; and
- A2: Biodegradation.

4.1.1 *Sub-column A1: Bioaccumulation*

4.1.1.1 *Introduction*

Bioaccumulation in aquatic organisms is a general term describing the complex process by which chemical substances are taken up into the body through all exposure routes (water, food and sediment). Bioaccumulation results in the presence of a substance(s) in the tissues of an organism. In practice, bioaccumulation is estimated by exposing fish or shellfish to a chemical in water under steady state conditions, i.e. by measuring bioconcentration from the water phase only and ignoring the influence of food or sediment. GESAMP is aware that such test methods may provide an inadequate simulation of what happens in the marine environment. However, bioconcentration tests do provide an accurate measure of the intrinsic tendency of a given substance to accumulate in living tissues and are therefore considered appropriate for use in the revised GESAMP hazard evaluation procedure.

Box 1

Guidance on the required quality standards of test reports

With regard to laboratory testing to generate data for the revised GESAMP hazard evaluation procedure, there is a strong preference for studies carried out under the OECD Principles of Good Laboratory Practice (GLP). Studies should be carried out to internationally standardized test guidelines, e.g. OECD or ISO test designs.

Care should be taken to ensure that:

- laboratories carrying out such studies are certified as being "in compliance" with OECD GLP or have appropriate alternative accreditation, e.g. for analytical chemistry or testing physical properties;
- the reports of such studies contain a quality assurance statement; and
- the tests meet the stated validity criteria of the appropriate test guidelines.

With respect to environmental end-points, detailed technical guidance is contained in annex IX of the GHS to assist in developing data for classifying substances as dangerous to the aquatic environment. The reader is referred to this document for a more detailed guidance on this issue.

A bioconcentration test (25) proceeds until a constant concentration of the substance has been reached in the tissue of the test organism, relative to the constant concentration in the water, through simultaneous uptake (e.g. by gill or epithelial tissue) and elimination. The exposure duration needed to reach a steady state will often depend on how hydrophobic/lipophilic the test substance is (see log Pow below). The bioconcentration factor (BCF) can be thus established accordingly.

An alternative experimental test method is available in which the test organisms are exposed to the chemical substance through their diets. The preference of the EHS Working Group is still for bioconcentration tests dosed through the water phase, unless the chemical is so hydrophobic as to make accurate dosing and analytical confirmation difficult, in which case a dietary study may provide useful data.

A surrogate for the measured (in vivo) bioconcentration factor (BCF), i.e. a chemical partition coefficient can be measured or estimated in a much simpler manner for organic chemicals. The living organism is replaced by n-octanol, which can be seen as representing the fatty tissues of the fish, in particular the phospholipid bilayers of the cell membranes. Usually expressed as the logarithm to the base 10, it is referred to as the log Kow or log Pow. It is one of the most important of a group of partition coefficients used to predict the

behaviour of chemicals in environmental compartments, e.g. Kd (soil/sediment adsorption constant), Koc (organic matter adsorption constant), Ka (water-air partition constant), etc. The log Pow does not apply to inorganic chemicals.

The log Pow is used by the EHS Working Group in three ways:

- to predict the potential of an organic chemical to bioaccumulate in fish tissues;
- to estimate baseline toxicity of organic substances to aquatic organisms. Baseline toxicity (26) data derived from the log Pow are routinely used for assessing the reliability of experimentally derived ecotoxicity test data (see Box 5 and section 4.2.1.3); and
- in the absence of reliable water solubility data, the log Pow can be used to provide estimates of aqueous solubility.

The internationally standardized methods available for measuring the log Pow of a chemical are the OECD Guidelines for the Testing of Chemicals 107 (27), 117 (28) and 123 (29). These are routinely used in the hazard assessment of chemicals. Additionally, there are two systems for calculating the log Pow from molecular fragment values (30) (31).

For values below 4, log Pow data generally provide sufficient information in their own right. However, for values above 4 to 6, measured log Pow data may underestimate bioaccumulation, whereas calculated log Pow data may overestimate. Therefore, at log Pow values of $\geq$4, a measured BCF is required to provide definitive information on the potential of a substance to bioaccumulate under steady state conditions. The measured BCF may ultimately result in a less severe hazard rating than the log Pow, as it allows for processes such as metabolism in the tissues of the organism, which may enhance the excretion of a substance.

Sub-column (A1) dealing with bioaccumulation therefore contains two sets of related information:

- **A1a:** the log n-octanol/water partition coefficient (log Pow)
  - estimated from fragmental constants; and
  - measured indirectly in the surrogate phases octanol and water.
- **A1b:** the measured BCF using fish, crustaceans or molluscs as test organisms.

For inorganic substances, the log Pow has no meaning. However, a label "Inorg." (for inorganic) is placed in the column to indicate that the substance

is inorganic and that no log Pow data can be generated. Bioaccumulation must then be based on an actual bioconcentration study.

Box 2

Guidance for experimentally measuring and calculating the log Pow

Several methods are available for calculating the log Pow. When commissioning log Pow tests, it is essential to ensure that the appropriate method for the compound in question is selected and that the detection limits of the analytical method are sufficiently low. Where very high log Pow values are expected, the slow-stirring method OECD No.123 is recommended, as described below. Surface active and easily emulsified compounds are generally difficult to test experimentally.

OECD No.107: The shake flask method

With this method, the chemical under study is placed in a two-phase octanol-water system and allowed to equilibrate by shaking. This method is suitable for compounds with log Pows of slightly below 0 (highly water soluble) to approximately 4 (moderately lipophilic). This method has the disadvantage that octanol droplets may enter the water phase, effectively emulsifying the test chemical in the wrong phase and disturbing the equilibrium.

OECD No.117: Reversed phase High Pressure Liquid Chromatography method

This is an indirect method, where the retention time on a C18 loaded HPLC column is used to estimate the log Pow. This method is particularly suitable for measuring log Pow values between 4 and 6 (highly lipophilic). Provided that suitably low analytical detection levels can be achieved and that all the other validity criteria can be met, this method may be extended beyond its originally intended range by adding additional standards with log Pow values above 6 to the recommended calibration series.

OECD No.123: Slow-stirring method

The slow-stirring method of de Bruijn et al. (32) is a direct method that uses a temperature controlled flask provided with gentle stirring to bring the chemical into equilibrium between the water and n-octanol phases. The water and n-octanol phases are periodically analysed, e.g. using appropriate HPLC or GC methods. This method has the advantage that compounds with a log Pow of up to 8 can be measured, depending on the limits of analytical detection available.

Generator column method

The generator column method of De Voe et al. (33) is an indirect method in which the compound is dissolved in n-octanol and coated onto an appropriate material contained in a generator column (e.g. HPLC column). The method is used to provide saturated solutions of the compound in water and is apparently suitable for highly hydrophobic substances up to log Pow values of 8.5. The disadvantage is that insufficient time may be available to reach equilibrium in all cases. The method is not internationally standardized.

Box 2 *(cont.)*

Calculating the log Pow using fragmental constants

It is very useful to be able to calculate the log Pow. In the case of surface active substances, using fragmental constants may be the only feasible way to estimate the log Pow. The hydrophobic fragmental constant method of Rekker and Mannhold (1992) and a comparable method provided by Hansch and Leo (1979) are both suitable for estimating log Pow values. The two methods are roughly equivalent. The US EPA EPI Suite computer based package contains a useful model (KOWWIN) for calculating the log Pow.

For sub-column A1b, bioconcentration data on fish are preferred, as frequently used and standardized test methods are available (see Box 3). However, data on other groups of organisms, such as crustaceans and molluscs, may be useful as additional information or where no other information is available. Although occasionally found in the literature, data on bioaccumulation in microalgae are not used by the EHS Working Group.

4.1.1.2 *Ratings*

For bioaccumulation, a rating scheme has been developed for sub-column A1 as shown in Table 2, below.

Table 2 – *Rating scheme for bioaccumulation*

Rating	Description	Criteria for log Pow	Criteria for BCF
0	No potential to bioaccumulate	<1, or > ca.7, or Mol. Wt. > 1000	No measurable BCF
1	Very low potential to bioaccumulate	≥1 – <2	≥1 – <10
2	Low potential to bioaccumulate	≥2 – <3	≥10 – <100
3	Moderate potential to bioaccumulate	≥3 – <4	≥100 – <500
4	High potential to bioaccumulate	≥4 – <5	≥500 – <4000
5	Very high potential to bioaccumulate	≥5 – < ca.7	≥ 4000

The substances most likely to pose a hazard to aquatic organisms through bioaccumulation typically have log Pow values ranging from 4 to approximately 8.

From Table 2 above, it can be seen that a log Pow of > ca.7 would generally lead to a "0" rating. The EHS Working Group considered that there was sufficient evidence to show that the majority of organic chemicals carried by ships with log Pow values of > ca.7 would show little tendency to bioaccumulate. However, while this is generally true for the particular set of chemicals transported in bulk by ships, it is recognized that many groups of highly persistent, bioaccumulative and toxic substances, e.g. PCBs and PCDDs, as well as other halogenated groups, form well-known exceptions to this rule. Van Leeuwen and Vermeire (34) discuss this topic in some detail in relation to log Pow estimation methods. Log Pow values of as high as 8.25 have been measured where associated bioaccumulation does take place. These are also often some of the most persistent substances in the environment.

Assessing the bioconcentration and bioaccumulation of metals in the marine environment presents some challenges due to the fact that grain size, solubility and, therefore, bioavailability of the substance are often complicating factors. Most available data have been derived from the testing of watersoluble metal salts. However, such data may not be applicable for assessing the bioaccumulation potential of non-soluble metals and metal complexes. Suitable experimental methods for assessing the aquatic toxicity of insoluble metals and metal compounds have been developed by the OECD and recognized by the GHS, as set out in annexes 9 and 10 of the manual. Moreover, some essential and even non-essential metals may be taken up by the organism through active transport, rather than simple diffusion processes. The environmental hazard of metals posed by bioaccumulation and toxicity remains difficult to estimate and interpret.

4.1.1.3 *Application*

Where the log Pow exceeds a value of 4, the substance is considered to "bioaccumulate to significant extent" unless the measured bioconcentration factor (BCF) can be shown experimentally to be less than a value of 500. Substances with BCF values in excess of 500 are also considered to bioaccumulate to a significant extent. Similar cut-off values are also contained in the GHS.

In general, measured BCF data, where available, are used to overrule log Pow data, provided that the study is scientifically sound and well documented. In the absence of a measured BCF value, the log Pow is used directly to provide a rating and for this reason, extrapolation of the log Pow to provide an estimate of the BCF is not necessary.

Box 3

Guidance for measuring bioconcentration in fish

The bioconcentration factor (BCF) is defined as the ratio (on a wet weight basis, normalized to a 5% fish fat content) between the concentration of the chemical in biota and the concentration in the surrounding water, at steady state. The BCF can thus be experimentally derived under steady state conditions, on the basis of measured concentrations. However, it can also be calculated as the ratio between the first-order uptake and elimination rate constants; a method which does not require equilibrium conditions. Different test guidelines for the experimental determination of bioconcentration in fish have been documented and adopted in the past. However, these have been consolidated in the OECD No. 305, entitled "Bioconcentration in fish: aqueous and dietary exposure".

In measuring the BCF, the focus is generally on the parent compound but in some cases, the metabolites may also be of concern. The use of radiolabelled test substances can facilitate the analysis of water and fish samples at low test substance concentrations. However, unless combined with a specific analytical method, the total radioactivity measurements potentially reflect the presence of the parent substance, as well as possible metabolite(s) and metabolized carbon, which have been incorporated in the fish tissue in organic molecules. As a result, BCF values determined by the measurement of radioactivity alone, tend to overestimate the presence of the parent compound in the fish tissues. Therefore, the use of specific analytical methods (with radiodetection) is strongly recommended. When using radiolabelled substances, the labelling is most often placed in the stable part of the molecule, for which reason the measured BCF value includes the BCF of the metabolites. Occasionally, it is the metabolite which is the most toxic and which has the highest bioconcentration potential. In such cases, measurements of the parent substance, as well as the metabolites, may be important for the interpretation of the aquatic hazard (including the bioconcentration potential) of such substances.

The recent revision of the OECD No. 305 includes bioconcentration via the dietary route, which may be more suitable for determining the bioaccumulation potential of substances with very low water solubility. Additionally, the traditional aqueous exposure method has been simplified by using only one concentration and less data points, provided certain criteria can be met. It has the advantage for animal welfare in that it uses less fish.

The majority of substances in bulk liquid maritime transport with very high log Pow values (>7) are generally presumed to be so insoluble in water as to pose no potential for bioaccumulation. However, where there is evidence to the contrary, the default "0" rating will be overridden and a measured or estimated log Pow will be used to derive a rating. This cut-off point was included to avoid classifying non bioaccumulating substances with high log Pow values, such as vegetable and animal oils (triglycerides).

Substances with molecular weights of >1,000 in bulk maritime transport are also assumed not to bioaccumulate (35) (36), as the molecular size is generally too large to pass through cell membranes.

Log Pow values are only applicable to organic substances, including organometals.

Experimentally derived bioconcentration factors may be more appropriate to assess the bioaccumulation potential of inorganic substances as well as some surfactants and organometallic substances.

Where mixtures are concerned, data on a worst case (i.e. highest) value of a range of components may be used to provide a rating, depending on the proportion of that component in the mixture. In general, a log Pow or BCF value will be required for all major components. Expert judgement will be applied in such cases.

4.1.2 *Sub-column A2: Biodegradation*

4.1.2.1 *Introduction*

Knowledge of the rate at which organic substances degrade in the aquatic environment is of great importance in determining their impact and ultimately in preventing biological effects. Metabolism by microbes is one of the most important routes of degradation of organic substances. Other degradation routes, e.g. abiotic, through hydrolysis and photolysis may also be of importance for some chemicals. With the exception of agricultural pesticides, there are little data available on the actual degradation rates of most chemicals in relevant environmental compartments, such as water and aquatic sediments, while data for degradation in the marine environment are particularly poor. As a result, an alternative "regulatory" approach is used. Tests designed to select rapidly biodegrading substances are used to group those that demonstrate the least environmental hazard. This is termed "ready biodegradability" and there is a wide range of freshwater tests, based on O_2 consumption, CO_2 evolution or dissolved organic carbon removal, with which it can be measured. However, as outlined in Box 4 and further described in annex IV, there are only two specific marine ready biodegradation test designs and biodegradation in freshwater can be quite different to the marine environment.

Photolysis, hydrolysis or other forms of rapid removal, e.g. by dissociation of inorganic substances in water, may also be taken into account as evidence of "ready" or rapid degradation. As IMO uses biodegradation (sub-column A2) for bulk liquid classification purposes, not only organic but also inorganic compounds are rated under this hazard profile sub-column. The latter are labelled as "inorganic" (abbreviated to "inorg.") in the GESAMP Composite List. A further subdivision of inorganic substances into readily dissolvable/

dispersible (R) or not-readily dissolvable/dispersible (NR) is included for some substances, although these parameters are not included in the composite list.

4.1.2.2 *Ratings*

The rating notation for sub-column A2 is shown in Table 3 and the pass and fail conditions are given in the section headed "Application" below.

Table 3 – *Rating scheme for ready biodegradability*

Description (organic substances)	**Rating**	**Description (inorganic substances)**	**Rating**
readily biodegradable	R	readily dissolvable/ dispersible	inorg. R
not readily biodegradable	NR	not readily dissolvable/ dispersible	inorg. NR

4.1.2.3 *Application to organic substances*

The biodegradation sub-column A2 refers to substances that are considered to be "readily biodegradable" if, in 28-day biodegradation studies, the following levels of degradation are achieved:

.1 in tests based upon dissolved organic carbon (DOC) dieaway: $\geq$70%; or

.2 in tests based upon oxygen depletion or carbon dioxide generation: $\geq$60% of the theoretical maxima; or

.3 where only chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) data are available, the ratio of BOD_5/ COD $\geq$0.5; or

.4 where other convincing scientific evidence is available to demonstrate that the substance can be degraded biotically and/or abiotically) in the aquatic environment to a level of >70% within a 28-day period.

The exact values of percentage biodegradation within 28 days should be reported, together with the methods that have been used.

Evidence from recognized estimation methods, which indicates that a compound may not be readily biodegradable, may provide sufficient evidence to avoid testing, in which case an (NR) rating may be assigned. Data generated by well-known estimation methods, such as the US EPA's BIOWIN set of models, may in some cases be acceptable for assigning the

rating "readily biodegradable" (R), provided that this is supported by the structure of the chemical and the results of BIOWIN's component (aerobic) models are all unequivocal.

Given the diversity of test methods available for determining ready bioavailability and the generally conservative nature of this criterion, GESAMP did not feel that the application of the "10-day window", an even more stringent rate function, recommended in the relevant OECD guidelines was justified.

It is strongly recommended that mixtures be approached on a modular basis, i.e. by testing their significant components separately. Biodegradation tests on mixtures only show mineralization of the most degradable components, while less degradable components remain behind.

Box 4

Guidance for measuring ready biodegradability

Biodegradation testing is complicated by considerable variability in microbial populations and the wide variety of freshwater test guidelines, some of which are more suitable than others. Annex IV contains an overview of the marine "ready" biodegradation test methods, and one freshwater method, which could be adapted to marine conditions. The terminology is further explained in the glossary.

Marine tests, e.g. OECD No. 306 (37) are preferred. There is evidence to show that biodegradation proceeds less rapidly in marine waters compared to freshwater environments (38). This may vary widely from location to location, e.g. polluted harbours and coastal waters may be well adapted to the biodegradation of chemicals, while such processes may be much slower under pristine oceanic conditions. The above method uses natural seawater as the only source of microorganisms. However, as nutrients are added to sustain microbial growth, this cannot be considered as a simulation of the natural environment. Freshwater tests, e.g. the OECD No. 301 A–F series (39), ISO 9439 (40), ISO 10707 (41) or EPA OPPTS equivalents, are acceptable, with limitations. All of these tests are inoculated with activated sludge from sources such as wastewater treatment plants (receiving domestic and not industrial effluent) and are thus expected to encourage biodegradation to a greater extent than the seawater design described above.

An acceptable alternative to the OECD No. 306 is the aerobic mineralization in surface water – simulation biodegradation test, OECD No. 309 (42) carried out with natural seawater and which allows testing of very low concentrations, under relatively natural conditions.

Inherent biodegradation tests, or wastewater treatment simulation tests, using microorganisms which have been pre-adapted to biodegrade chemical substances, are not considered to be sufficiently representative of the marine environment to be acceptable.

4.1.2.4 *Application to inorganic substances as required by IMO*

Under sub-column A2, inorganic substances are also considered, as IMO uses the A2 sub-column for pollution categorization and ship-typing purposes, therefore requiring a rating for all substances. Inorganic substances are therefore given a rating of R if they are readily dissolvable/dispersible in water.

4.2 Column B: Aquatic Toxicity

Column B has two sub-columns, one representing acute aquatic toxicity (B1), and the other containing information on chronic aquatic toxicity (B2).

Aquatic toxicity is generally expressed as the LC_{50}, EC_{50} or IC_{50}. In acute tests, the LC_{50} is usually determined for fish and crustaceans, the EC_{50} (immobility) for the commonly used freshwater crustacean *Daphnia sp.*, while the IC_{50} or EC_{50} (reproduction and/or growth) generally applies to microalgae. Most test guidelines describe how water soluble substances should be tested. However, many substances carried in bulk by ship are poorly soluble, defined for this purpose as having a water solubility of <1 mg/l, and two approaches are available for testing this type of substance.

With poorly soluble, pure substances, the water solubility is first determined accurately. The substance is then tested using a concentration series at and below the saturation level in water. Where no acute toxicity can be measured within the limit of solubility of the substance in water, the result of the test is expressed as being:

> "greater than x mg/l and therefore above the limit of solubility in water"

and a rating of '0' is given, where x is the near-saturated concentration of the substance in the test water. Should toxicity be observed, then the result is calculated and expressed in the normal way as an $LC/EC/IC_{50}$ and an appropriate rating assigned. Confirmation of the exposure concentrations using chemical analysis is essential.

Where mixtures are concerned, differential solubility of the components may make conventional testing and analysis very difficult and a different approach may need to be taken. A series of water accommodated fractions (WAFs, see annex V) are prepared by stirring excess amounts of the test substance separately in water (at a uniform speed) for a period of 16 to 24 h to allow an equilibrium to be achieved (in reality, a true equilibrium is seldom demonstrated). The phases are allowed to separate for approximately 4 h and the test water (less the test substance) is tapped directly into the test vessels and the test organisms immediately introduced. In such cases, the test results are expressed as the "loading rate" (LL_{50}/EL_{50} and IL_{50}), rather than the exposure concentration. Critics of this method note that the most

toxic component may be underestimated by the integral result derived for the mixture as a whole. However, this is the reality in the event of a chemical spill. The EHS Working Group considers that the methodology provides sufficient indication of the intrinsic hazard of mixtures to be useful.

In general, data from freshwater aquatic toxicity tests are acceptable for evaluation by GESAMP. The molecular (partitioning) processes governing bioaccumulation and non-specific "baseline toxicity" effects are generally the same for marine and freshwater organisms. However, there are some differences in the effects caused by specific groups of chemicals, e.g. for organometallic compounds, metal ions, ammonia, amines and acids in seawater, as opposed to freshwater. Toxicity of dissociating/reactive substances may be influenced by pH and the buffering capacity of seawater may reduce exposure and thereby the potential for aquatic toxicity.

4.2.1 *Sub-column B1: Acute aquatic toxicity*

4.2.1.1 *Introduction*

In order to rate the hazard posed by chemical substances to aquatic organisms, the most practical solution available is still considered to be the use of acute toxicity test data. Data relating to organisms representing the middle to upper levels of an aquatic food chain, e.g. crustaceans and fish, are used, in addition to microalgae, which represent primary producers at the base of the food chain.

It is recognized that the standardized tests carried out according to international guidelines do not represent what will necessarily happen when substances of low solubility, low density and high volatility are spilled or discharged at sea. However, it is important that all substances be considered on the same basis, namely that of their intrinsic toxicity under standardized and controlled conditions.

Table 4 – *Revised GESAMP rating scheme for acute aquatic toxicity*

Rating	Description	LC/LL_{50}, EC/EL_{50}, IC/IL_{50} (mg/l)
0	Non-toxic	>1000
1	Practically non-toxic	>100 – ≤1000
2	Slightly toxic	>10 – ≤100
3	Moderately toxic	>1 – ≤10
4	Highly toxic	>0.1 – ≤1
5	Very highly toxic	>0.01 – ≤0.1
6	Extremely toxic	≤0.01

4.2.1.2 *Ratings*

The acute aquatic toxicity ratings cover the range from >1000 mg/l down to <0.01 mg/l, as shown in Table 4. The bands of toxicity separate groups of substances on a log scale, in order to reflect the hazards associated with:

- substances with limited toxicities, but that can result in a significant volume accidental release (e.g. LC/EC_{50} 100–1,000 mg/l);
- the acute toxicity bands of the GHS (10–100, 1–10 and ≤1 mg/l);[10]
- substances which by their very high (0.1–0.01 mg/l) or extreme (≤0.01 mg/l) acute toxicity may be hazardous in small quantities.

All of these bands of toxicity are used in regulating substances under MARPOL Annex II (bulk liquid substances).

Box 5

Guidance for measuring acute aquatic toxicity

Acute aquatic toxicity tests are carried out commercially by many contract research laboratories. It is advisable to select reputable laboratories with experience in testing difficult substances, as many substances transported in bulk by sea fall into this category due to poor solubility (see annex V), volatility, tendency to solidify at ambient temperatures, etc.

Fish

The appropriate test for measuring the acute aquatic toxicity to marine fish is OECD No. 203 (43). This is an established and flexible guideline allowing the use of many freshwater and marine species. A small estuarine fish, the sheepshead minnow *Cyprinodon variegatus*, has generally been found suitable. Other fish species are also acceptable, as indicated in the above guideline. The OECD No. 204, 14-day prolonged toxicity study, is not recommended, as it is too long for an acute study and too short for a chronic study.

As alternative methods become internationally standardized, taking into account the concerns related to animal welfare, the EHS Working Group may consider data generated with fish embryos.

[10] Acute class I of the GHS contains all substances with an LC/EC_{50} of ≤1 mg/l. The revised GESAMP hazard evaluation procedure adds three extra hazard bands. Apart from the reasons given above, this is intended to enable IMO to consider in detail the categorization of mixtures. The GHS uses M-factors (M for mixture) to achieve the same purpose.

Box 5 (cont.)

Crustaceans

Tests with marine crustaceans can be carried out according to the ISO 14669 guideline (44). The recommended species are the copepod *Acartia tonsa* and the mysid shrimp *Mysidopsis bahia* (45). Other well-established guidelines, covering additional marine crustaceans, may also be acceptable. Where freshwater data is already available, data on the water flea Daphnia magna according to OECD No. 202 (46) is generally acceptable.

Microalgae

Microalgal toxicity tests can best be carried out under the ISO 10253 (marine) (47), ISO 8692 (freshwater) (48) or OECD No. 201 (freshwater) (49) guidelines. The ISO standards generally provide more practical guidance. All of the above guidelines have been updated relatively recently. In addition, advice on the toxicity testing of difficult substances using microalgae, including volatile and poorly soluble chemicals, is given in ISO Test No.10634 (50).

Testing poorly soluble pure substances and mixtures

Annex V to this document contains guidance on methods for exposing organisms to poorly soluble mixtures, whose components may exhibit a variety of different behaviours in water. For further advice on this topic, the reader is referred to the guidance provided by organizations such as ISO, European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) (51) and OECD (52).

Analytical determination of exposure concentrations

Acute aquatic toxicity tests should be accompanied by analytical evidence showing that exposure to a particular concentration of the test substance has occurred and has been appropriately maintained. Where mixtures are concerned, this may be problematic. A useful approach to testing may be to use Total Organic Carbon analysis of the test media. The reader is referred to the specific guidance contained in the relevant OECD guidelines and to the above guidance documents.

4.2.1.3 *Application*

Data from the following three standard tests will generally be used:

- 96 h LC/LL_{50} fish tests;
- 48 to 96 h $LC/LL_{50}/EC/EL_{50}$ crustacean tests; and
- 72 to 96 h $EC/EL_{50}/IC/IL_{50}$ microalgal growth inhibition tests.

Where only one result each for the three groups of organisms is available and the data are of acceptable quality, the lowest LC_{50} or EC_{50} (i.e. from the test showing the highest acute toxicity) will be used to assign the toxicity rating. The use of a weight of evidence approach for larger data sets for assignment

of ratings by read across is considered in section 3.9 and is applied by the EHS Working Group, as appropriate.

Data from either standard freshwater or marine aquatic toxicity tests are used for assigning ratings. The processes governing the expression of toxicity in freshwater and marine organisms are generally similar. Baseline toxicity upon exposure to non-polar organic substances, i.e. the accumulation of substances in the phospholipid bilayer of the cell membrane until saturation is reached and the cell dies, is common to both freshwater and marine organisms. This also probably holds true for polar organic substances. However, reactive substances may show altered toxicity in seawater by comparison to freshwater. In such cases, marine data are preferred and may provide a more realistic assessment of the toxicity of substances to marine organisms.

Toxicity data generated with organisms other than fish, crustaceans and microalgae, in particular other marine taxa, may also be acceptable.

4.2.2 *Sub-column B2: Chronic aquatic toxicity*

4.2.2.1 *Introduction*

Chronic toxicity addresses the impacts of long-term exposure of aquatic organisms and is a core component of hazard evaluation in the marine environment, as it considers the influence of:

- operational discharges from ships in heavily used shipping lanes, particularly near specially protected marine areas; and
- accidental spills from ships, where the timescales involved may be longer than expected, e.g. where the substances form slicks that do not break up and readily disperse (see section 4.5), bearing in mind the potentially large volumes involved.

The GHS relies on measured chronic aquatic toxicity data by preference. However, to reach a GHS classification, chronic toxicity data is always combined with evidence of non-rapid or rapid degradation or, in the absence of measured chronic data, acute data is combined with evidence of non-rapid degradation or bioaccumulation to significant extent. By contrast, for the GESAMP hazard profile, the hazard end-points are kept separate. This is because the EHS Working Group is tasked with evaluating the intrinsic hazard of substances and is not involved in classification of products. However, the separate GESAMP ratings can be combined to classify substances under the GHS.

The acute and chronic GESAMP aquatic toxicity scales have been given an independent rating system (as does the GHS) and are treated as separate effects.

Box 6

Guidance for measuring chronic aquatic toxicity

Fish

Suitable tests for measuring chronic toxicity to fish include the fish early life stage test (OECD No. 210) (53) and the 28d fish juvenile growth test (OECD No. 215) (54). Equivalent national or regional test guidelines may also be acceptable. It should be noted that the OECD No. 212 (55) test with egg and sac-fry stages may not provide enough information for the purpose of providing a chronic rating. For investigating such specific end-points as endocrine disruption or reproductive disturbance in fish, recent test guidelines such as the OECD Nos. 229 (56), 230 (57) and 234 (58) may be used. For the purposes of assigning a rating for chronic aquatic toxicity, the latter is the most suitable.

Crustaceans

A suitable standardized test for determining chronic toxicity to marine crustaceans is described in the US EPA 850.1350 guidelines (59) for *Mysidopsis bahia*. An equivalent test that is still in the process of international standardization is a reproduction test with the calanoid copepod *Acartia tonsa* (60). Further information on reproduction and development testing with calanoid and harpacticoid copepods can be found in the report of an OECD validation study (61). Data from freshwater species, e.g. the 21d *Daphnia magna* reproduction test (OECD No. 211) (62) is also commonly used. Chronic tests with crustaceans generally begin with juveniles and continue through maturation and reproduction. For mysid shrimp, 28 days are sufficient for maturation and the production of broods. Observational test end-points include time to first brood, number of offspring produced per female, growth and survival.

Microalgae

Microalgal toxicity tests can best be carried out under the ISO 10253 (marine), ISO 8692 (freshwater) or OECD No. 201 (freshwater) guidelines. The ISO standards generally provide more practical guidance. All of the above guidelines have been updated relatively recently.

In addition, advice on the toxicity testing of difficult substances using microalgae, including volatile and poorly soluble chemicals, is given in ISO Test No. 10634.

Analytical determination of exposure concentrations

Chemical analysis to measure the exact exposure concentrations is essential in the case of all chronic tests to show that exposure to a particular concentration of the test substance has occurred and has been appropriately maintained. Where mixtures are concerned, this may be problematic. The reader is referred to the specific guidance contained in the relevant OECD guidelines and to the above guidance documents.

4.2.2.2 *Ratings*

The ratings for chronic aquatic toxicity are placed in a separate sub-column, using a log scale based primarily on the "No Observed Effect Concentration" (NOEC), as shown in Table 5 below. The NOEC is defined as the highest concentration tested at which no significantly different effects from the control population are observed (e.g. survival, reproduction or growth). Where a NOEC is not available, an EC10 calculated from the experimental effect data may be substituted. Box 6 lists suitable test methods, including their exposure times and end-points. As with the GHS, substances with a chronic NOEC of >1 mg/l are not considered to be chronically toxic.

Table 5 – *Ratings for chronic aquatic toxicity*

Rating	Description	No observed effect concentration (mg/l)
0	Negligible	>1
1	Low	>0.1 – ≤1
2	Moderate	>0.01 – ≤0.1
3	High	>0.001 – ≤0.01
4	Very high	≤0.001

4.2.2.3 *Application*

Chronic aquatic toxicity data are not routinely requested from industry. However, the EHS Working Group of GESAMP may request such data in the following cases:

- for poorly soluble substances where the acute toxicity is difficult to estimate accurately, or where it is reported that the substance is "non-toxic" within the limits of solubility in water;
- where definite chronic effects are suspected, e.g. on growth, development or reproduction, e.g. from structural alerts, or from mammalian toxicity data;
- where a specific mechanism of toxicity is expected, e.g. with pesticides; or
- substances that are known to degrade slowly and/or bioaccumulate.

The choice of test organism will generally be based on the most sensitive group among the available acute tests.

4.3 Column C: Acute Mammalian Toxicity by ingestion, skin contact and inhalation

4.3.1 *General remarks*

Acute toxicity refers to adverse effects that occur following a single oral or dermal administration of a chemical substance, or uninterrupted inhalation exposure of less than 24 hours, usually for 4 hours.

Column C addresses the potential acute toxicity of chemicals to humans. The hazards related to ingestion, skin contact and inhalation exposure routes are considered under three sub-columns (C1, C2 and C3).

LD_{50} or LC_{50} values have been used for many decades to indicate the dose leading to severe, life threatening or acutely toxic effects and such data usually form the basis by which chemicals are compared with each other regarding acute hazards for human health. Historically, such numerical data are used by many regulatory systems as one of the most important hazard classification criteria for the protection of human health. With the introduction of the GHS and modern testing procedures by the OECD, the term Acute Toxicity Estimate (ATE) is now used instead, referring to a range of test results or extrapolations equivalent to LD_{50}/LC_{50} values. The rating system is therefore based on numerical dose or concentration values from animal tests, expressed as ATE values.

The limitations of using data from acute toxicity tests with mortality as the single end point are recognized, in particular when no other detailed information can be examined. These issues have been extensively discussed in a variety of forms and publications. It is generally accepted that, in principle, there should be considerably more aspects evaluated for defining an acute hazard than the lethal dose alone. While most toxicological knowledge on this topic derives from animal experiments, human experience, e.g. instances of accidental poisoning, should also be taken into account. All available information is therefore considered together by the experts and ratings are given on the basis of the total weight of evidence.

There has been growing public concern about the use of laboratory animals for lethal dose testing for many years. The OECD has already published alternative guidelines to the classic LD_{50} tests, aimed at a reduction in both the numbers used and the suffering of test animals. Alternatives to in vivo animal testing based on Quantitative Structure-Activity Relationships (QSAR) or the use of in vitro test systems have been published in the scientific literature, but as yet are either insufficiently effective or have not been sufficiently validated. The development of such alternative methods will be closely monitored by GESAMP and the content of this chapter may be

amended as appropriate in the future. The estimation of inhalation toxicity, using a combination of acute oral and/or acute dermal, as well as skin and eye irritation and corrosion, is addressed below.

4.3.1.1 *Ratings*

The ratings, based on ranges of ATEs for oral, dermal and inhalation exposures are shown in Table 6 below.

Table 6 – *Rating system for acute mammalian toxicity by ingestion, skin contact and inhalation (sub-columns C1, C2 and C3)*

Rating	Relative Hazard	C1 Oral ATE (mg/kg)	C2 Dermal ATE (mg/kg)	C3 Inhalation ATE (mg/l/4 hr)
0	Negligible	>2000	>2000	>20
1	Slight	>300 – ≤2000	>1000 – ≤2000	>10 – ≤20
2	Moderate	>50 – ≤300	>200 – ≤1000	>2 – ≤10
3	Moderately high	>5 – ≤50	>50 – ≤200	>0.5 – ≤2
4	High	≤5	≤50	≤0.5

4.3.1.2 *Application*

The quality and consistency of the underlying data are of great importance. Generally, reliable data from human exposure will be given precedence over animal data. However, negative evidence from human exposure will not normally be used to override positive data from standard tests in experimental animals.

Values from mammalian species and the most susceptible sex are used, except where there is convincing evidence that toxicity in humans may be different.

In general, for interspecies extrapolation, detailed models, e.g. based on metabolism or body surface, are not taken into account and dose values in "mg/kg" are used directly.

The revised GESAMP Hazard Evaluation Procedure does not include a separate toxicity class from 2000 to 5000 mg/kg, as provided by the GHS, as this is not currently required under MARPOL for categorizing chemical substances.

The ratings for acute inhalation toxicity are orientated towards animal experiments using atmospheres consisting of vapours or mists. GESAMP evaluates data on substances known to form mist, vapour or gas on a case by case basis, bearing in mind the cut-off values contained in the GHS.

Where high quality inhalation studies, conducted with pure mists/aerosols without any exposure to vapour, are employed, cut-off values for mists/aerosols, as presented in the GHS, may be applied, e.g. suitable for substances which have a very low vapour pressure.

4.3.1.3 *Interpreting acute hazard data*

The rating of a hazard should not be interpreted as a risk assessment. Risk must take into consideration the potential toxicity (hazard) and the exposure in a specific situation. The acute toxicity rating defines, in effect, the relative potential for severe poisoning. In this way, the oral toxicity is evaluated, although swallowing of chemicals carried as cargo is not foreseen as an exposure route on board ships. Likewise, for inhalation risk, more factors than just the ATE or LC_{50} would need to be taken into account, including, for example, the saturated vapour concentration. It is up to risk managers to define whether hazards alone, or risks including exposure parameters, need to be considered, in order to select appropriate risk management options. A number of regulatory systems for transport and plant licensing are based on hazard evaluation only (63).

Under accidental conditions on board ships, bursting pipes could create aerosols, while in the aftermath of an accidental discharge, mist may be generated by waves on the sea surface. In such cases, the estimated hazard could correspond to the situation and the potential exposure. On the other hand, under normal operational conditions, there may not be any aerosol generated in tanks, and liquids with very low vapour pressure will not even create vapours. Under such circumstances, the inhalation risk could be significantly lower than indicated by the hazard identification on its own and further data may need be taken into consideration, e.g. vapour pressure of the cargo at the transport temperature or the saturated vapour pressure, in order to apply appropriate risk management measures.

4.3.2 ***Sub-column C1: Acute oral toxicity***

Standardized tests are preferred for evaluation (see Box 7). In evaluating a chemical whose toxic potential is unknown, it is often useful to conduct a range-finding study or a limit test. The ATE or LD_{50} would be reported as "greater than", if no death of experimental animals is observed within 14 days. Such results can be fitted into the rating scale and will be evaluated accordingly. The GESAMP ratings are consistent with Acute Toxicity (oral) Hazard Categories 1 to 4 of the GHS.

4.3.3 ***Sub-column C2: Acute dermal toxicity (skin contact)***

Experience has shown that chemicals that are non-toxic by the oral route are generally also non-toxic by the dermal route. Experience has also shown

that orally toxic chemicals are also potentially toxic by dermal application. Such facts may enable experts to estimate the toxic potential in the case of missing data, thus allowing an estimated rating to be shown in brackets. Range-finding studies and limit tests are taken into account, as outlined for oral toxicity testing above. The GESAMP ratings are consistent with Acute Toxicity (dermal) Hazard Categories 1 to 4 of the GHS.

4.3.4 *Sub-column C3: Acute inhalation toxicity*

4.3.4.1 *Inhalation toxicity criteria*

The criteria for inhalation toxicity are based on ATE or LC_{50} data relating to 4 h exposures in rats and such information is preferred where available. Where LC_{50} data relating to 1 h exposure is available, these values can be divided by 4 to be considered equivalent to the LC_{50} (4 h).

The GESAMP ratings are generally based on cut-off values introduced by the GHS under Acute Toxicity (inhalation) Hazard Categories 1 to 4 for vapour exposure.

Conversion from "ppm" to "mg/l" should be based on the formula:

$$\text{mg/l (20°C)} = \frac{\text{ppm} \times \text{molecular weight}}{24 \times 1000}$$

4.3.4.2 *GESAMP inhalation toxicity extrapolation method*

In practice, experimental data for evaluating acute inhalation toxicity is often not submitted to EHS and may not be available for the following reasons:

.1 it is deemed unethical to carry out animal experiments on substances known to cause undue pain and suffering to animals; or

.2 the physical or chemical properties of the chemical are such that relevant tests cannot be carried out.

In such cases, the GESAMP EHS Working Group endeavours to provide a reliable estimate of acute inhalation hazard, in order to be able to complete the hazard profile and to advise relevant authorities of the hazard believed to be presented by inhalation of the chemical.

The technique devised by the EHS Working Group to provide an estimate of the acute inhalation hazard is termed the 'GESAMP inhalation toxicity extrapolation method'; this provides a consistent and acceptable estimate of acute inhalation hazard based on other data that is usually more readily available, namely:

1. the oral and dermal acute toxicity;

2. the irritant/corrosivity potential to the skin and eye; and

3. any information regarding inhalation toxicity to aerosols, mists, etc. of the chemical itself or of analogous chemicals recognized to have similar bio-reactive properties.

The approach adopted is presented in Table 7 below. The highest acute dermal or oral hazard rating is identified in the left column. Reading across a given row, the corresponding highest rating for skin or eye irritation is identified in the middle column and the resulting estimated rating for acute inhalation toxicity is provided in the right column.

Table 7 – *The GESAMP acute inhalation toxicity extrapolation method based on route to route and end-point extrapolation*

Highest acute oral and/ or dermal rating	Highest skin and/or eye irritation rating	Estimated acute inhalation toxicity rating
0	0	0
	1	1
	2	2
	3	3
1	0	1
	1	2
	2	
	3	3
2	0	2
	1	
	2	
	3	3
3	0	3
	1	4
	2	
	3	
4	0	4
	1	
	2	
	3	

Estimated inhalation toxicity ratings derived from this method are shown in the GESAMP hazard profile contained within brackets „( )“, to identify them as estimates.

In some cases the ratings shown in brackets may overestimate the potential for poisoning by inhalation, particularly for substances with low saturated vapour pressure. Consequently, a decision may be taken by IMO to utilize other methods for defining specific occupational health protection requirements on board ships (risk management).

Box 7

Guidance on acute oral, dermal and inhalation toxicity testing

Over the last several decades, test guidelines for assessing acute toxicity to mammals have been consolidated and published by the OECD, to the extent that other guidelines are now seldom used. However, older published test data derived from testing procedures other than those listed (including the use of different mammalian species) should be evaluated before new testing is considered. Such existing data are equally valid for evaluating hazard ratings, provided the experimental procedures are sufficiently well documented and can be evaluated independently.

New testing should be based on OECD guidelines and performed in accordance with the OECD Principles of Good Laboratory Practice (GLP).

Acute oral toxicity

- Wherever possible, testing for acute oral toxicity should be based on standardized 14-day post-dosing observation in rats. The recommended methods are: OECD No. 420, Acute oral toxicity – fixed dose procedure (64)
- OECD No. 423, Acute oral toxicity – acute toxic class method (65)
- OECD No. 425, Acute oral toxicity – up-and-down procedure (66)

Following withdrawal of the OECD No. 401 guideline for Acute oral toxicity, based on concerns for animal welfare, GESAMP no longer recommends its use for determining the LD_{50}.

Acute dermal toxicity

For measuring dermal toxicity, standardized LD_{50} tests with rats or rabbits are preferred, using 24-hour occlusion with two weeks of observation. The recommended guideline is OECD No. 402, Acute dermal toxicity (67).

Acute inhalation toxicity

Wherever possible, ratings for inhalation toxicity should be based on standardized 14-day post-dosing observation tests in rats. The recommended guidelines are OECD No. 403, Acute inhalation toxicity (68) and OECD No. 436, Acute inhalation toxicity – Acute toxic class method (69).

Practical experience in inhalation toxicity testing shows that the test atmosphere will, in most cases, not just consist of vapour, but of a mixture

of liquid (mist) and vapour. Test results which are based on exposure to a saturated vapour and which show less severe effects than exposure to mists or aerosols are also taken into consideration. In such circumstances a hash mark (#) is appended to the EHS product entry to indicate that the hazard may be less severe for vapour exposure than for exposure to mist/aerosol.

4.4 Column D: Irritation, Corrosion and Long-term Health Effects

This column considers the harmful effects of chemical substances on skin, eyes and mucous membranes resulting from irritant and/or corrosive substances, and also potential long-term health effects.

The skin, eyes and mucous membranes of humans may become exposed to chemical substances, either by physical contact or inhalation in a wide variety of situations, e.g. in the work environment on board ship, on the dockside, when swimming in the ocean or during maritime rescue operations. The effects of chemicals resulting from direct contact with skin or eyes are rated under sub-columns D1 and D2, respectively. A numerical rating is given based on test data or human experience. Long-term health concerns are indicated in sub-column D3.

4.4.1 *Sub-column D1: Skin irritation/corrosion*

4.4.1.1 *Introduction*

Toxic insults to the skin can significantly affect the health and well-being of an individual. Chemicals may cause irritation and/or corrosion of skin through several mechanisms. In most cases, several pathological pathways may occur at the same time. However, the classification of damage due to irritation or corrosion of the skin is based on morphology rather than on measures of specific mechanisms.

Skin irritation is measured as the production of reversible damage to skin following the application of a chemical substance for 4 hours. In the past, data on skin irritation has also been provided by dermal exposures over 24 hours. Exposures of 4-hour duration are preferred, but data from 24-hour exposures can also be accepted and this latter data is used directly, without extrapolation, whilst recognizing that this may err on the side of caution.

Skin corrosion is measured as the production of irreversible damage to skin, e.g. visible necrosis, following the application of a chemical substance for up to 4 hours. The rapidity of producing an adverse effect, within 3 minutes, 1 hour or 4 hours, can indicate the degree of corrosivity.

Data for the evaluation of skin irritation/corrosion can be obtained from human experience, animal experiments or from in vitro assays. In respect to in vitro methodologies, the rating of skin irritation/corrosion is based only on validated test methods. However, all other tests and information are evaluated to derive an estimated rating.

For the purpose of assigning a rating in sub-column D1, data are collected from current databases, the literature and test reports. These sources may reflect experiments carried out during a wide time period and performed under variable quality surveillance. Sometimes the test may not have been carried out according to present day standards or evaluated under the current scoring systems. In such cases a cautionary approach is taken and a higher rating may be assigned. Ratings which are estimated by expert judgement are shown in brackets "( )".

4.4.1.2 *Ratings*

The ratings and descriptions used for sub-column D1 are shown in Table 8 below.

Table 8 – *Rating system for skin irritation and corrosion*

Rating	Description	Signs	GHS Category
0	Not irritating	No clinical signs and/or inflammation	---
1	Mildly irritating	Mild erythema with or without oedema (rapidly reversible)	Mild Irritant Category 3
2	Irritating	• Marked erythema • Obvious and marked oedema • Other signs of local injury	Irritant Category 2
3	Severely irritating or corrosive	• Severe irritation indicating local tissue damage • Full-thickness skin necrosis, applied when exposure time is not reported	Corrosive Category 1
3A	Corrosive	Full-thickness skin necrosis following exposure between 1 hr and 4 hr	Corrosive Category 1C
3B		Full-thickness skin necrosis following exposure between 3 min and 1 hr	Corrosive Category 1B
3C		Full-thickness skin necrosis following exposure up to 3 min	Corrosive Category 1A

4.4.2 Sub-column D2: Eye irritation

4.4.2.1 *Introduction*

Eye irritation is the production of changes in the eye following application of a chemical substance to the anterior surface of the eye, which are fully reversible within 7 or 21 days after application. Serious eye damage is the production of tissue damage in the eye, or serious physical decay of vision, following a similar application to the eye, which is not fully reversible within 21 days of application.

Testing the effects of chemicals on the eye is generally carried out by exposing the eye of experimental animals to a small amount of solid or dissolved chemical substance. The eye and the surrounding tissue are then inspected at various time intervals, e.g. after 1, 24, 48 and 72 hours. Effects on the cornea, iris and conjunctiva are noted and scoring systems have been developed in order to summarize the effects. Draize and co-workers introduced the best known of these in 1944 (70). Since then, changes have been introduced in study design and scoring, and some in vitro methods have been validated and are acceptable. If classification is based on extrapolation, e.g. based on skin corrosivity, extreme pH (<2 or >11.5), or evidence from analogous chemicals, the ratings are shown in brackets.

4.4.2.2 *Ratings*

The ratings and descriptions used in sub-column D2 are given in Table 9 below.

Table 9 – *Ratings for eye irritation and corrosion*

Rating	Description	Clinical signs	GHS Category
0	Not irritating	No clinical signs and/or inflammation	–
1	Mildly irritating	Mild conjunctival hyperaemia with or without chemosis, reversible within 7 days	Irritant Category 2B
2	Irritating	Marked conjunctival hyperaemia, chemosis, corneal injury – all reversible within 21 days	Irritant Category 2A
3	Severely irritating, with irreversible corneal injury	Severe conjunctoblepharitis, chemosis, corneal injury or similar effects not fully reversible within 21 days	Irritant Category 1

Box 8

Guidance on acute dermal and eye irritation and corrosion tests

Results from all previous testing and from human experience are evaluated, but new testing should be based on OECD guidelines and performed under Good Laboratory Practice (GLP).

Acute dermal irritation and corrosion

The recommended tests are the OECD No. 404, Acute dermal irritation/corrosion test (71) and the in vitro alternative tests, OECD Nos. 430 (72), 431 (73), 435 (74) and 439 (75).

Acute eye irritation

The recommended tests are the OECD No. 405, Acute eye irritation test (76) and the in vitro alternative tests OECD Nos. 437 (77) and 438 (78), using ex vivo organs from bovines and poultry respectively.

4.4.3 *Sub-column D3: Long-term health effects*

4.4.3.1 *Introduction*

There are a wide variety of chemical hazards to human health besides those listed in sub-columns C1, C2, C3, D1 and D2. Long-term health effects, as a result of either single or repeated exposure, are listed in Table 10 below.

4.4.3.2 *Rating*

The GHS considers several of these hazards under its Specific Target Organ Toxicity (STOT) classification. Others, such as sensitization, carcinogenicity, mutagenicity and reprotoxicity, are defined separately here and in the GHS.

Unlike the GHS, no sub-divisions of classification for these long-term health effects are distinguished in the ratings. Instead, a simple representation of the nature of the hazard is presented using a letter symbol.

The absence of one of the hazards in sub-column D3 should not be considered to indicate that a particular chemical does not possess this property. This could either be based on the results of standard testing showing no positive effect, or could be due to the absence of any standard testing or lack of epidemiological data.

Table 10 – *Long-term health effects covered under sub-column D3 and the corresponding GHS categories*

Notation in sub-column D3	Hazard end-point	Description	GHS Category
C	Carcinogenicity	Chemicals which have been shown to induce or increase the incidence of cancer	Category 1 for Carcinogens
M	Mutagenicity	Cause a permanent change in the amount or structure of genetic material in cells	Categories 1 and 2 for Germ Cell Mutagens
R	Reprotoxicity	Cause adverse effects on reproductive ability or capacity, or on the development of offspring	Category 1 for Reproductive Toxicants
Ss	Skin Sensitization	Cause specific skin hypersensitivity or allergy following skin contact	Category 1 for Skin Sensitizers
Sr	Respiratory Sensitization	Cause specific hypersensitivity of the airways, or asthma, following inhalation	Category 1 for Respiratory Sensitizers
A	Aspiration	Lung injury or chemical pneumonia following aspiration of a chemical through the oral or nasal cavity into the trachea or lower respiratory system	Category 1 for Aspiration Toxicity
T	Specific Target Organ Toxicity following single or repeated exposure	Significant changes which affect the morphology or biochemistry of tissues or organs; organ dysfunction up to death	Categories 1 and 2 for Specific Target Organ Toxicity Single (STOT-SE) or Repeated Exposure (STOT-RE)
N	Neurotoxicity	Like T, but specific for effects on the central nervous system or senses	
I	Immunotoxicity	Like T, but specific effects on the function of the immune system	

4.4.3.3 *Application*

Carcinogenicity (C)

The term carcinogenicity denotes substances or mixtures that are presumed to induce cancer or to increase its incidence in humans. Evidence to substantiate the notation 'carcinogenicity' in sub-column D3 should be available from epidemiological studies and/or from well-conducted studies in experimental animals. Chemicals are rated as 'C', based on the GHS criteria (Category 1A or 1B) for known or presumed human carcinogenicity, and evaluation by the International Agency on Research of Cancer (IARC group 1 or group 2a). In principle, the EHS Working Group bases its ratings on the evaluation of reliable evidence and on expert judgement, in particular those classifications developed by WHO experts within the IARC. "Suspected" human carcinogens are not covered by the GESAMP 'C' rating.

Mutagenicity (M)

A mutation is a permanent change in the amount or structure of the genetic material in a cell. The term mutation applies to genetic changes both for somatic cells and for germ cells that may give rise to subsequent adverse changes at the phenotypic level. The term mutagenic denotes substances or mixtures that can give rise to an increased occurrence of mutations in vivo, in populations of cells and/or organisms. Evidence to substantiate a rating 'M' is normally provided from studies conducted in vivo on mammalian somatic cells or germ cells. As such, the scoring is consistent with GHS category 1 and 2 for germ cell mutagenicity.

Reprotoxicity (R)

Reprotoxicity (or reproductive toxicity) includes adverse effects on sexual function and fertility in adult males and females or on the development of the offspring. The rating 'R' in sub column D3 includes substances for which there is reliable evidence from human experience or from experimental animals of an adverse effect on reproductive ability or capacity, or on development of the offspring in the absence of other toxic effects. As such, the scoring is consistent with GHS category 1 and 2 for reproductive toxicity. Substances identified as "suspected" human reproductive toxicants as defined by the GHS are not covered by the notation 'R'.

Skin Sensitizer (Ss)

The term skin sensitizer denotes substances or mixtures which can induce a condition of hypersensitivity or allergy in individuals following skin contact (contact sensitizer). Evidence to substantiate a rating 'Ss' in sub-column D3 should be available from appropriate studies, using experimental animals

or from human experience. The criteria used for the evaluation of test results are consistent with those listed in the GHS for Hazard Category 1 for skin sensitizers.

Respiratory Sensitizer (Sr)

The term respiratory sensitizer denotes substances or mixtures which can induce a condition of hypersensitivity of the airways, or asthma, in individuals following inhalation. Evidence to substantiate a rating of 'Sr' in sub-column D3 is normally based on human experience, most often seen as asthma, but other reactions such as rhinitis/conjunctivitis or alveolitis, having the clinical character of an allergic response, are also considered. As in the cases of asthmatic attacks or respiratory distress, immunological mechanisms may not necessarily be involved and do not have to be demonstrated. Evidence may also be available from appropriate studies using experimental animals; however, to date, recognized animal models have not been validated. The criteria used for the evaluation of test results are consistent with those listed in the GHS for Hazard Category 1 for respiratory sensitizers.

Aspiration hazard (A)

Severe acute effects or chemical pneumonia may be caused by aliphatic, alicyclic and aromatic hydrocarbons of low viscosity, as well as other substances that, based on clinical experience, may cause damage to the airways or lungs after direct aspiration or after being swallowed. The criteria used for the evaluation of test results are consistent with those listed in the GHS for Hazard Category 1 for aspiration hazards.

Specific Target Organ Toxicity (T)

Classification depends upon the availability of reliable evidence that single or repeated exposure to the substance has consistently produced a long-term toxic effect in humans or in experimental animals, including significant changes affecting the function or morphology of a tissue or organ, or has produced serious changes to the biochemistry or haematology of the organism, and these changes are relevant to human health. The criteria used for the evaluation of test results are consistent with those listed in the GHS for Hazard Categories 1 and 2 for *Specific Target Organ Toxicity*.

Rating with 'T' includes lung injury after inhalation, injury to the central nervous system and/or peripheral nervous system, and also adverse effects on the immune system. It should be noted that neurotoxicity (N) and immunotoxicity (I) fall within STOT under the GHS. However, in terms of classification, N and I are used independently.

Neurotoxic (N)

The term neurotoxic denotes substances or mixtures which are capable of causing injury to the central nervous system (brain and spinal cord) and/or peripheral nervous system (nerves arising from the brain and spinal cord). Neurotoxicity may appear as the result of single or repeated exposure, even to very low doses/concentrations. Evidence to substantiate a notation of "neurotoxic" in sub-column D3 should be available from epidemiological studies and/or from well-conducted and appropriate studies in experimental animals.

Immunotoxic (I)

The term immunotoxic denotes substances or mixtures which are capable of causing injury to the immune system and interfere with the body's defence mechanisms. Evidence to substantiate a rating of "immunotoxic" in sub-column D3 should be available from epidemiological studies and/or from well-conducted and appropriate studies in experimental animals.

4.5 Column E: Interference with other uses of the sea

Column E covers the hazards to other uses and users of the sea from operational discharges and accidental releases of substances. The results are set out in three sub-columns as shown in Table 11 below.

Table 11 – *Column E: Interference with other uses of the sea*

Sub-column	Potential interference with:	Criterion
E1	Fisheries	Tainting of seafood
E2	Wildlife and bottom habitats	Physical behaviour of substances in seawater: • Effects of viscous, slick-forming substances on marine wildlife • Effects of sinking substances on benthic habitats, e.g. smothering of the seabed
E3	Use of coastal amenities	Hazards to humans using beaches, coastlines, onshore and offshore installations and harbours.

This aspect differs markedly from other hazard classification systems such as the GHS. Given the large volumes of substances transported by ship, it is considered necessary to provide a separate criterion that enables IMO to regulate operational discharges of bulk liquid substances, which might not be identified by classical hazard parameters such as toxicity or bioaccumulation.

These hazard end-points may also provide information that can be of use during a maritime emergency when substances are spilled, or are likely to be spilled, into the marine environment.

4.5.1 *Sub-column E1: Tainting of seafood*

4.5.1.1 *Introduction*

Chemical taint

Tainting, in this context, is the process whereby seafood acquires an off-flavour following exposure of the food organism to chemical substances. Despite depuration and excretion of the substance, once the exposure has ceased, e.g. after a spill has dispersed, the flesh of the organism continues to give an off-flavour or smell. In 1982, GESAMP defined taint as:

> *"a foreign flavour or odour in the organisms induced by conditions in the water to which the organisms are exposed".*

Although best known as a result of oil contamination, tainting has been induced by inadequate aquaculture practices and effluent disposal, although scientific studies have also shown that tainting is regularly produced naturally in seas without any relevant marine pollution.

Laboratory tests for tainting by chemical substances

In the late 1980s, GESAMP and ECETOC (79) developed separate test guidelines for measuring taint. Poels et al. (80) reported that the ECETOC method was tested in a collaborative study, which demonstrated its imprecision at the desired threshold levels. Published data on tainting substances are scarce in the scientific literature and, regrettably, little testing has been done on pure chemicals with which to build up a database since GESAMP first introduced this criterion. Experimental studies are available on approximately 40 chemical substances and, as a result, there has been little opportunity for laboratories to gain experience, or for the method to be standardized. A further disadvantage is that, understandably, the testing of industrial chemicals using human tasting panels is strictly regulated in many countries, especially where the long-term toxicity of such chemical substances is unclear.

Tainting by oil spills

Many cases of tainting have been observed as a result of heavy pollution following accidental spillage from oil tankers or, as a result of continuous sources of pollution from harbour or river areas (81). However, mineral oils, as covered under Annex I of MARPOL, are outside the scope of the present report.

Box 9

Guidance on laboratory tests for estimating tainting

For the purposes of detecting chemical taint, tainting tests have been shown to be insufficiently precise at the required exposure level of 1 mg/l. While they are no longer required by IMO, such tests may be of use to detect taint in seafood organisms exposed following oil spills.

Tainting is generally measured in a triangular tasting test in which a panel of 15 to 20 human tasters assess groups of three samples of cooked seafood, one of which has been exposed to the chemical at an appropriate concentration, the other two being blank controls. The fish is first exposed to the chemical in water for 24 h, then killed, filleted and steamed in tightly wrapped foil.

The available methods are:

- GESAMP
- ECETOC
- ISO 4120 (82) is generally followed for setting up the triangular tasting tests with panels of human volunteers.

The ECETOC recommendation is similar to that issued by GESAMP but it allows the fish to be kept after exposure in non-contaminated water for excretion or metabolism.

Generally, the qualitative detection of taint is not the method of choice following oil spills. Chemical analysis is used instead as a more accurate alternative giving quantitative results. Residue limits for many chemical groups are defined by FAO and adopted in many countries as quality standards for seafood. However, tainting measurement is still recommended by the FAO/IMO "Guidance on Managing Seafood Safety During and After Oil Spills" (83). Additionally, Whittle et al. (84) reported that in the aftermath of the **Braer** oil tanker accident and subsequent spillage off the Shetland Islands in 1993, the assessment of taint proved to be a high-capacity, rapid and sensitive screening method for the dominant Alkyl (C1–C4) naphthalene contamination of seafood.

Regulatory standards for tainting

Chemical tainting of seafood had been considered by MARPOL in order to prevent "harm to amenities or other legitimate uses of the sea" and is thus taken as a criterion for classifying the pollution category of bulk liquid substances. Annexes II and III of MARPOL, the IBC Code and the IMDG Code have been revised in this respect. Tainting as a criterion for classifying bulk

liquid substances and as a criterion for the definition of Marine Pollutants is no longer used.

Conclusion

Tainting has been deleted by IMO as a regulatory criterion for classifying chemical substances for transport purposes. The GESAMP Composite List was checked in 2000 to ensure that all ratings are supported by sufficient evidence. Substances that have been rated on this basis will continue to be listed in sub-column E1 but no further evaluations related to tainting will be performed.

4.5.2 *Sub-column E2: Behaviour of chemicals in the marine environment*

4.5.2.1 *Introduction*

The tendency of a spilled chemical to form a slick, to dissolve, to evaporate or to sink and blanket the seabed determines, to a large extent, its potential to exert physical effects on marine wildlife and benthic habitats. The Bonn Agreement Behaviour Classification System (85) evaluating the short-term behaviour of chemicals spilled at sea has been used as the basis for assessing such physical effects. This system is also utilized within the regional pollution prevention agreements for the North, Baltic and Mediterranean Seas, and is designed to facilitate cooperation in dealing with marine pollution emergencies, as well as by IMO (86) (87) (88). The system was slightly modified by GESAMP to meet the requirements of MARPOL Annex II and the IBC Code, to include viscosity as an additional end-point when evaluating "persistent floating" substances and this is further described below.

4.5.2.2 *Bonn Agreement Behaviour Classification System for chemicals spilled into the sea*

Chemicals that are spilled into the sea behave in different ways, depending on their properties and the prevailing environmental conditions. In principle, spilled chemicals can float, evaporate, dissolve or sink but in reality, they often show complex behaviour patterns when released in the marine environment. Based on information on the physical and chemical properties of substances (physical state, density, vapour pressure and solubility), an indication of the behaviour pattern following release into the water can be obtained.

The Behaviour Classification System contained in the Bonn Agreement Counter Pollution Manual classifies chemicals according to their physical behaviour when spilled into the sea. The classification system covers gaseous, liquid and solid chemicals. The main principle of the system is to characterize spilled chemicals as: evaporators, floaters, dissolvers and sinkers.

From this basic categorization and from other details regarding their physical properties, the chemicals are classified in the following 12 property groups.

Table 12 – *Groups classified by physical state and properties*

G	Gas	**GD**	Gas that dissolves
E	Evaporator	**ED**	Evaporator that dissolves
F	Floater	**FE**	Floater that evaporates
		FD	Floater that dissolves
		FED	Floater that evaporates and dissolves
D	Dissolver	**DE**	Dissolver that evaporates
S	Sinker	**SD**	Sinker that dissolves

Grouping of chemicals by their physical properties

The property groups of the Bonn Agreement Behaviour Classification System are defined according to the physical state of the substance (gas, liquid, solid) and by certain cut-off values of vapour pressure (v.p.), density (d), and solubility (s). The method of classifying chemicals by physical property cut-off values is shown in Figure 2.

Physical state of the substance

In this context, gases are chemicals that boil below ambient temperature at normal atmospheric pressure of 100 kPa. This means that gases are those chemicals with vapour pressures above 100 kPa at ambient temperature. The meaning of liquids and solids refers to the state of aggregation at ambient temperature and atmospheric pressure (100 kPa). Liquids are chemicals that boil above ambient temperature at 100 kPa, but melt below ambient temperature (melting point $<$ ambient temperature). Solids are chemicals that melt above ambient temperature at 100 kPa (melting point $>$ ambient temperature).

Density

The relative density of a chemical related to seawater makes it possible to predict whether it floats or not. The density of seawater is approximately 1025 kg/m^3.

Vapour pressure

Vapour pressure is only used for evaluating liquid substances. Below 0.3 kPa, a floating substance is not considered to evaporate and above 3 kPa evaporation is rapid. A dissolved substance will evaporate if the vapour pressure is higher than 10 kPa.

Solubility

The criteria adopted for solubility differ according to the physical state of the substance. Substances are considered insoluble when the solubility is ≤0.1 % for liquids and ≤10% for solids. Dissolution predominates when solubility is ≥5% for liquids and ≥100% ("totally miscible") for solids.

Figure 2 shows the principles of the Bonn Agreement Behaviour Classification System for chemicals likely to be spilled into the sea. By this classification system, whole groups of chemicals (see Table 14) can be covered by the same response strategies, thus simplifying preparedness measures for the response to an accidental release of chemicals.

Figure 2 – *Bonn Agreement Behaviour Classification System of accidentally spilled chemicals according to their physical state and properties*

<table>
<tr><td colspan="5">A – GASES (Vapour Pressure > 101.3 kPa at 20°C)</td></tr>
<tr><td>Behaviour groups</td><td colspan="2">G</td><td colspan="2">GD</td></tr>
<tr><td>Solubility</td><td colspan="4">0% 10%</td></tr>
<tr><td colspan="5">B – FLOATING LIQUIDS (Density < Seawater)</td></tr>
<tr><td>Vapour Pressure</td><td colspan="4">SEBC groups</td></tr>
<tr><td rowspan="3">10 kPa
3 kPa
0.3 kPa</td><td colspan="2" rowspan="2">E</td><td>ED</td><td>DE</td></tr>
<tr><td>FE</td><td colspan="2">FED</td><td rowspan="2">D</td></tr>
<tr><td>F</td><td colspan="2">FD</td></tr>
<tr><td>Solubility</td><td colspan="4">0.1% 1% 5%</td></tr>
<tr><td colspan="5">C – SINKING LIQUIDS (Density > Seawater)</td></tr>
<tr><td>Behaviour groups</td><td>S</td><td>SD</td><td colspan="2">D or DE
(if VP >10kPa)</td></tr>
<tr><td>Solubility</td><td colspan="4">0.1% 5%</td></tr>
<tr><td colspan="5">D – FLOATING SOLIDS (Density ≤ Seawater)</td></tr>
<tr><td>Behaviour groups</td><td>F</td><td>FD</td><td colspan="2">D</td></tr>
<tr><td>Solubility</td><td colspan="4">10% 100%</td></tr>
<tr><td colspan="5">E – SINKING SOLIDS (Density > Seawater)</td></tr>
<tr><td>Groups</td><td>S</td><td>SD</td><td colspan="2">D</td></tr>
<tr><td>Solubility</td><td colspan="4">10% 100%</td></tr>
</table>

4.5.2.3 *Ratings*

Ratings and the associated criteria for determining potential physical effects on wildlife and on benthic habitats are given below in Table 13. As noted above, GESAMP has added an additional behaviour class by combining floating properties with high viscosity in order to predict longer lasting or persistent slicks. These substances are given a rating of 'Fp', according to the criteria set out below.

Table 13 – *Revised GESAMP hazard profile ratings for determining potential effects on wildlife and benthic habitats*

Rating	Description and criteria	Physical effects	Examples
F	Floating substance, not likely to evaporate or to dissolve quickly • Density: ≤ sea water (1025 kg/m^3 at 20°C) • Vapour pressure: ≤0.3 kPa • Solubility: ≤0.1% (for liquids) ≤10% (for solids)	Effects on marine wildlife (e.g. smothering, immobilization)	• iso-octanol • octanoic acid • undecene
Fp	Persistent slick forming substance • All of the criteria for a floating substance, as well as: • Viscosity: >10 cSt at 20°C	Effects on marine wildlife (e.g. smothering, immobilization)	• pine oil • soyabean oil • dodecyl alcohol • tallow
S	Sinking substance that would deposit on the seabed, not likely to dissolve quickly • Density: > seawater (1025 kg/m^3 at 20°C) • Solubility: ≤0.1% (for liquids) ≤10% (for solids)	Effects on benthic habitats (e.g. blanketing and anoxia of the sediments, poisoning, immobilization)	• perchloro-ethylene • phenol • dichloro benzene

The guidelines for categorization of Noxious Liquid Substances in MARPOL Annex II use only the F (floater), Fp (persistent floater) and S (sinker) ratings. However, for the benefit of other users of the GESAMP hazard profiles, the other physical behaviour categories are also included in sub-column E2 (see Table 14).

For mixtures, which will have a range of values for each of the relevant properties, a value giving a worst case rating will generally be used.

Table 14 – *Bonn Agreement Behaviour Classification System Groups*[11]

Groups	Behaviour of the substance	Examples
G	Gas	• propane • butane • vinyl chloride
GD	Gas/Dissolves	• ethylamine • ethylene oxide
E	Evaporates	• benzene • toluene • hexane
ED	Evaporates/Dissolves	• methyl-tert-butyl ether • vinyl acetate • ethyl acrylate
FE	Floats/Evaporates	• octane • xylene
FED	Floats/Evaporates/Dissolves	• butyl acetate • butyl acrylate
FD	Floats/Dissolves	• aniline • di butyl ether
D	Dissolves	• sulphuric acid • butyl alcohol
DE	Dissolves/Evaporates	• acetone • acrylonitrile • propylene oxide
SD	Sinks/Dissolves	• dichloromethane • benzyl acetate

4.5.2.4 *Application*

The behaviour groups are defined according to the physical state of the substance (e.g. gas, liquid, solid) and its density, vapour pressure and solubility, which should be given at a temperature of 20°C.

For mixtures, where a range is given for the viscosity at the carriage temperature, an estimate is made to establish the maximum of that range at 20°C. Conversion methods, such as that given by Gambill (89), may be used in such cases.

[11] The first letter refers to the primary behaviour of a substance while subsequent letters describe subsidiary behaviour(s). These ratings are given for the benefit of other users of the hazard profiles.

Using the above method, which is based on the exponential relationship between dynamic viscosity (cP) and temperature, the viscosity of most chemicals at any temperature can be estimated if the viscosity is known at one temperature.

Example: Polybutene (density = 0.83) has a reported kinematic viscosity of 125 cSt at 37°C, equivalent to 104 cP (125 × 0.83 = 104 cP or mPa.s) at 37°C. Its dynamic viscosity is estimated to be 280 cP at 20°C giving a kinematic viscosity of 337 cSt (280 ÷ 0.83 = 337 cSt) at 20°C.

For solutions (substances dissolved in water), e.g. ammonium sulphide solution (45% or less), the following selected properties of seawater are used to determine a behaviour category for the substance:

- Melting point –1.91°C
- Solubility 100%
- Vapour pressure 2000 Pa (nominal value based on seawater)

The solubility of a substance in water is often indicated in handbooks of physical properties by a range of vague expressions, e.g. soluble, slightly soluble, poorly soluble, etc. Table 15 is based on a review of the interpretation of solubility phrases from data sources where the descriptive term is qualified by a measured value or range. This interpretation is only used as a guide in estimating the solubility range for purposes of assigning a rating to sub-column E2 as the interpretations differ markedly from, for example, those used in ecotoxicology (see section 4.2) or analytical chemistry.

Table 15 – *Terminology for describing solubility*

Solubility for the purpose of sub-column E2	**Descriptive terminology commonly used in chemical handbooks**
≥5% for liquids ≥100% for solids	Infinite; completely soluble; soluble in all proportions; miscible; very soluble; soluble
0.1 – 5% for liquids 10 – 100% for solids	Partially soluble; moderately soluble; slightly soluble
≤0.1% for liquids <10% for solids	Insoluble; barely soluble; immiscible; almost insoluble; poorly soluble

It is recognized that the presence of dissolved salts or minerals in water leads to moderate decreases (and in a few cases an increase) in solubility.

However, since, for most substances, data for solubility in saline water are not available, the solubility quoted for pure water at 20°C is used.

Box 10

Guidance for measuring solubility in water, relative density, vapour pressure and viscosity

Solubility in water

Lyman et al. (90) defined the solubility of a substance as the maximum amount that will dissolve in water at a specified temperature (usually 20°C). Aqueous concentrations are usually expressed in terms of weight per weight (g/kg) or weight per volume (g/l). The OECD No.105 (91) recommends one of two methods, i.e. the shake flask method or the column elution method. The former is suitable for solubilities above 10 mg/l, while the latter is suitable for solubilities below this value.

Relative density

The density of a substance is the quotient of its mass and its volume and is expressed in kg/m^3. The OECD No.109 (92) indicates that a wide variety of methods can be used and provides guidance on their applicability.

Vapour pressure

Vapour pressure is defined (93) as the pressure exerted when a solid or a liquid is in equilibrium with its own vapour. At thermodynamic equilibrium, the vapour pressure is a function of temperature only. Vapour pressure can be measured in several ways depending on the expected range. The OECD No.104 (94) lists seven different methods. The static, effusion and gas saturation methods are suitable for low melting point solids and liquids over a wide range of possible vapour pressures. Vapour pressure is measured in Pascals (Pa).

Viscosity

Viscosity is a measure of a fluid's resistance to flow and the OECD No.114 (95) provides a working definition of viscosity (see Glossary). Viscosity is measured in milliPascals per second (mPa/s). Three principles are used for measuring the dynamic viscosity of Newtonian liquids, and most of the available methods, with the exception of the "flow cup", appear to be suitable for measuring a wide range of viscosities:

- flow under gravity through a capillary (capillary viscometer or flow cup);
- shearing of the fluid between concentric cylinders, cone-plate and parallel plate (rotational viscometer);
- dynamic viscosity can be measured by movement of a ball in a vertical or inclined liquid-filled cylindrical tube (e.g. a rolling ball viscometer, or a drawing ball viscometer).

Box 10 (cont.)

Only the rotational viscometer method is suitable for non-Newtonian liquids.

Viscosity units and conversion

- Dynamic viscosity: 0.01 poise (P) = 0.01 g/cm/s = 1 mPa/s
- Kinematic viscosity: 1 Centistoke (cSt) = 1 mm^2/s

Kinematic viscosity (cSt) is the ratio of viscosity (cP) to density (d) at a given temperature, i.e. cSt = cP/d

4.5.3 *Sub-column E3: Interference with the use of coastal amenities*

4.5.3.1 *Introduction*

Interference with coastal amenities refers to the potential of a substance to interfere with activities in coastal waters, including ports or estuaries, fishing, usage of beaches, appearance of an area, the health of human coastal populations, marine mammals and the preservation of living resources.

Sub-column E3 is supported by data on human health hazards and physical properties from all of columns C and D as well as sub-column E2 and flammability.

One of the physical properties considered is the flammability of the substance and for the purposes of determining ratings in sub-column E3, the following substances are considered to be flammable:

- liquids with a flashpoint below 23°C;
- liquids with a flashpoint between 23°C and 60°C that are floaters and also show evaporative (FE) or evaporative and dissolving (FED) behaviour.

4.5.3.2 *Ratings*

The ratings in sub-column E3 are presented in Table 16 below. It should be borne in mind that these ratings and their associated hazard warnings are based on the intrinsic properties of the chemical and are intended as guidance only. They are not intended as a risk assessment. They are designed to aid in decision-making with respect to closure of beaches in the event of chemical contamination.

Additional factors related to a spill situation, such as weather and hydrodynamic conditions, quantity spilled, local conditions, etc., must be evaluated by competent spill response authorities before a decision is taken to, for example, implement the closure of a beach.

Table 16 – *Revised GESAMP hazard rating scheme for evaluating "interference with coastal amenities"*

Rating	Relative interference	Description	Interpretation	Hazard warning
0	None	1 is not a floater; **and** 2 does not pose any known health hazards	1 E2 is not F or Fp; **and** 2.1 C1, C2 and C3 = 0; **and** 2.2 D1 and D2 = 0; **and** 2.3 D3 is blank	None
1	Slightly objectionable	1 is a floater; **and/or** 2 is slightly acutely toxic; **and/or** 3 is mildly irritant to skin and/or eyes	1 E2 = F; **and/or** 2 C1 and/or C2 and/or C3 = 1; **and/or** 3 D1 and/or D2 = 1	Warning issued but no closure of amenities
2	Moderately objectionable	1 is a persistent floater; **and/or** 2 is moderately acutely toxic; **and/or** 3 is irritating to skin and/or eyes; **and/or** 4 has long-term health effects other than carcinogenicity, mutagenicity or reprotoxicity; **and/or** 5 is highly flammable; **and/or** 6 is moderately flammable and is a floater with evaporative properties	1 E2 = Fp; **and/or** 2 C1 and/or C2 and/or C3 = 2–3; **and/or** 3 D1 and/or D2 = 2; **and/or** 4 D3 contains Ss, Sr, T, A, N, or I; **and/or** 5 Flashpoint <23°C; **and/or** 6 Flashpoint 23°C to 60°C and E2 = FE or FED	Warning issued and possible closure of amenities
3	Highly objectionable	1 is highly acutely toxic; **and/or** 2 is severely irritant or corrosive to skin or eyes; **and/or** 3 is carcinogenic, mutagenic or reprotoxic; **and/or** 4 is a floater or persistent floater with associated health effects	1 C1 and/or C2 and/or C3 = 4; **and/or** 2 D1 or D2 = 3, 3A, 3B, or 3C; **and/or** 3 D3 contains C, M or R; **and/or** 4 E2 = F or Fp and D3 contains Ss, Sr, T, A, N, or I	Warning issued leading to the closure of amenities

5 – Glossary

Activated sludge Biomass produced in the aerobic treatment of wastewater by the growth of bacteria and other microorganisms in the presence of dissolved oxygen. It usually consists of small flocs (the sludge) made up of pieces of organic matter surrounded or activated by colonies of microorganisms.

Acute aquatic toxicity Adverse effects on aquatic organisms that occur rapidly as a result of short-term exposure to a chemical or physical agent. A chemical is considered acutely toxic if by its direct action it kills 50% or more of the exposed population of test organisms such as fish or crustaceans in a relatively short period of time, such as 24-96 h.

Acute toxicity Adverse effects in humans or mammalian test animals produced by single exposure to a substance.

Acute Toxicity Estimate (ATE) Refers to a dose range or extrapolated dose leading to lethal effects in mammals, equivalent to an LD_{50} or LC_{50}.

Allergen Any substance which induces a state of, or brings on, manifestations of allergy; a hypersensitive reaction involving an immune-mediated response.

Aspiration hazard Any substance which, if inhaled into the respiratory tract during swallowing or vomiting of the substance, will cause respiratory tract injury because of its severe irritancy or corrosivity, or cause a granulomatous reaction because of its insolubility and persistence in the respiratory tract.

Baseline aquatic toxicity Baseline toxicity is the (theoretical) aquatic toxicity exerted by a substance due to the simplest mode of toxic action, i.e. non-polar narcosis, a process whereby the phospholipid bi-layers of cell membranes become saturated with the substance, causing the cell to die.

Bioaccumulation General term describing a process by which chemicals are taken up by aquatic organisms directly from water as well as from exposure through other routes, such as consumption of food and sediment containing the chemicals.

Biochemical oxygen demand (BOD) A measure of the rate at which molecular oxygen is consumed by microorganisms during oxidation of organic matter. The standard test is the 5-day BOD test, in which the amount of dissolved oxygen required for oxidation over a 5-day period is measured. The results are measured in mg of oxygen/l (mg/l).

Bioconcentration	A process by which there is a net accumulation of a chemical directly from water into aquatic organisms resulting from simultaneous uptake (e.g. by gill or epithelial tissue) and elimination.
Bioconcentration factor (BCF)	A term describing the degree to which a substance can be concentrated in the tissues of an organism in the aquatic environment as a result of exposure through the water phase. At steady state during the uptake phase of a bioconcentration test, the BCF is a value equal to the concentration of a substance in one or more tissues of the exposed aquatic organisms divided by the average exposure water concentration of the chemical in the test.
Biodegradation	The transformation of a substance resulting from the complex enzymatic action of microorganisms (e.g. bacteria, fungi). It usually leads to disappearance of the parent structure and to the formation of smaller chemical species, some of which are used for cell anabolism.
Carcinogen	The term carcinogen denotes a chemical substance or mixture which induces cancer or increases its incidence. Substances which are known to induce benign or malignant tumours in well-performed experimental studies on animals are also considered to be presumed or suspected human carcinogens, unless there is strong evidence that the mechanism of tumour formation is not relevant for humans.
Chemical oxygen demand (COD)	A measure of the oxygen equivalent of the organic matter in wastewater susceptible to oxidation by a strong chemical oxidizing agent (e.g. potassium permanganate; see also BOD).
Chemosis	A swelling of the conjunctiva due to accumulation of tissue fluid.
Chronic aquatic toxicity	Adverse effects on aquatic organisms that occur largely from continuous long-term exposure to one or more chemicals, but where the exposure time covers only a portion of the life cycle (lifespan) of the aquatic species tested. The effects are more often the consequence of repeated or continuous long-term exposures.
Chronic toxicity	Effects resulting from repeated exposure to a substance for the lifespan of the species, or the greater part thereof.
Coastal amenity	Beach, mudflat, wharf, boardwalk or any other feature of the coastline considered of public value.
Conjunctiva	Mucous membrane which lines the anterior chamber of the eye.
Cornea	The clear, transparent portion of the eye covering the iris and lens.

Corrosive	Capable of causing erosive destruction of tissues.
Cut-off value	Indicates the point on the scale of a given hazard criterion, e.g. acute aquatic toxicity, or skin irritation and corrosion, chosen to represent a perceived degree of hazard. The cut-off values are generally chosen to represent quantitative degrees of hazard and spaced at order of magnitude intervals, or are qualitative in nature, reflecting a descriptive degree of injury or potential damage.
Dermal toxicity	Systemic toxic effects produced as a result of a substance being absorbed across the skin.
Dermatitis	Inflammation of the skin evidenced by itching redness and various skin lesions.
Dissolved Organic Carbon (DOC)	That part of the organic carbon in the water which cannot be removed by specified phase separation, for example by centrifugation at 40000 m s^{-2} for 15 min or by membrane filtration using membranes with pores of 0.2–0.45 µm diameter.
EC_{50}	Median effective concentration. The concentration of a substance which produces a 50% response in the defined end-point. The EC_{50} should be cited for a specific exposure period.
EL_{50}	Effective loading rate 50%. The loading rate in excess of the aqueous solubility of a substance or mixture at which a 50% effect is caused in tests with aquatic organisms following exposure to water accommodated fractions of the substance (see annex V).
(Hazard) End-point	A discrete hazard to aquatic life or human health, related to one or more intrinsic properties of a substance, which can be experimentally measured, or evaluated, e.g. on the basis of human experience.
Erythema	Excess of reddening of a tissue due to increased flow of blood.
Immunotoxic	Capable of causing injury to the immune system and interference with body defence mechanisms.
Inherent biodegradability	Biodegradation of the test compound under enhanced conditions, either with a preadapted innoculum or a high level of activated sludge. The tests may be either static or flow-through, e.g. simulating a wastewater treatment process.
IC_{50}	Inhibition concentration 50%. A point estimate of the chemical concentration that would cause a given percent reduction (e.g. IC_{50}) in a non-lethal biological measurement of the test organisms, such as reproduction or growth. The IC should be cited for the specific exposure period.

IL_{50}	Inihibition load 50%. The loading rate in excess of the aqueous solubility of a substance or mixture at which a 50% inhibition of population growth is measured in tests with microalgae following exposure to water accommodated fractions of the substance (see annex V).
Irritant	Capable of causing a local inflammatory response.
LC_{50}	Lethal Concentration 50%. The concentration, in air or in a solution, which causes 50% mortality of the test species. It is calculated from the incidence of mortality at various concentrations to which different groups of the test species are exposed. Since mortality will depend on the time of exposure, the LC_{50} should be cited for the specific exposure period.
LD_{50}	Lethal Dose 50%. The amount (dose) of test substance that causes 50% mortality of the test species. It is calculated from the incidences of mortality at various doses given to different groups of the test species. It is usually expressed as mg (or g) of test substance per g or kg of body weight of the test species. Also referred to as the median lethal dose.
LL_{50}	Lethal load 50%. The loading rate in excess of the aqueous solubility of a substance or mixture at which a 50% mortality is caused in tests with aquatic organisms following exposure to water accommodated fractions of the substance (see annex V).
Log Pow	See n-octanol-water partition coefficient.
Mixture	Mixtures or solutions composed of two or more substances which are not chemically combined and which cannot be separated by physical methods.
Mutagen	A substance capable of causing molecular injury to the genetic constitution.
Necrosis	Death of areas of tissue or bone surrounded by healthy parts.
Neurotoxic	Capable of causing injury to the central nervous system (brain and spinal cord) and/or peripheral nervous system (nerves arising from the brain and spinal cord). Delayed neurotoxicity refers to injury to the nervous system following a single exposure, but for which there is a significant latent period between exposure and the appearance of signs of a neurotoxic effect.
Newtonian fluids	Fluids are distinguished as Newtonian if the viscosity is constant for different rates of shear that does not change with time, e.g. water or gasoline. The viscosity of non-Newtonian fluids either varies with the rate of shear or varies with time, even though the rate of shear is constant, e.g. some mineral slurries (behaving like quicksand).

No Observed Effect Concentration (NOEC)	The highest concentration of a substance in a toxicity test that has no statistically significant adverse effect on the exposed population of test organisms compared with the controls. When derived from a life cycle or partial life cycle test, it is numerically the same as the lower limit of the Maximum Acceptable Threshold Concentration (MATC), also called no observed adverse effect level (NOAEL).
n-Octanol-water partition coefficient (Kow or Pow)	The ratio of a chemical's solubility in n-octanol and water at steady state; also expressed as P. The logarithm of P or Kow (i.e. log P or Kow) is used as an indication of a chemical's propensity for bioconcentration by aquatic organisms.
Oedema	Swelling of a tissue due to excess accumulation of tissue fluid.
Primary biodegradation	The structural change (transformation) of an organic chemical compound by microorganisms resulting in the loss of a specific property.
Ready biodegradability	70% removal of dissolved organic content (DOC) and 60% removal of theoretical oxygen demand (ThOD) or theoretical carbon dioxide ($ThCO_2$) production (for respirometric methods), reached within a 10 d window in 28 d using non-adapted bacterial innocula.
Risk	The likelihood of harm occurring, e.g. when exposure of an organism to a substance is considered in conjunction with hazard data (*Hazard x Exposure = Risk*). If either hazard or exposure can be minimized, the risk or likelihood of harm will be reduced.
Reproductive toxicity	Injury to the male or female reproductive system, interfering with the propagation of the species.
Reprotoxic	Similar to the above. A substance causing adverse effects on reproductive ability or capacity, or on the development of offspring.
Sensitization	Exposure to the substance results in stimulation of the immune system, resulting in a state of hypersensitivity to the substance. Sensitization by skin contact results in local allergic responses. Sensitization by inhalation (respiratory sensitization) can cause asthma or similar symptoms of respiratory distress.
STOT	Specific Target Organ Toxicity, as defined in the GHS.
Sub-chronic toxicity	Effects resulting from repeated exposure to a substance for 10% to 15% of the lifespan of the species. For rodents this is about three months.
Substance	For the purposes of this guidance, 'substance' refers to pure and technically pure substances as well as mixtures to facilitate maritime regulatory requirements, noting that this deviates from the GHS definition for substances.

Systemic toxicity	Adverse effects produced by a substance (or conversion products) after absorption into, and circulation by, the bloodstream. Systemic effects occur in tissues remote from the site where the substance comes into contact with the body, and from where it is absorbed.
Tainting	Taint is defined as a foreign flavour or odour in marine organisms, induced by conditions in the water to which the organisms are exposed.
Teratogen	A substance capable of causing injury to the conceptus and resulting in permanent structural and/or functional malformations.
Theoretical Oxygen Demand (ThOD)	The theoretical maximum amount of oxygen required to oxidize a chemical compound completely, calculated from the molecular formula, expressed in this case as mg oxygen required per mg or g test compound.
Toxic	Capable of causing adverse effects, detrimental to the survival or normal functioning of the individual.
Viscosity	Defined by OECD No. 114 as *"the measure of the property of a fluid substance of absorbing a stress"*, in which reference, definitions of dynamic and kinematic viscosity can also be found. More simply put: the resistance of a fluid (liquid or gas) to a change in shape, or movement of neighbouring portions (e.g. layers) relative to one another, i.e. viscosity denotes opposition to flow.
Water Accommodated Fractions	The fractions of a mixture dissolved in water following a fixed period of high-energy stirring, at a loading rate of test substance well in excess of saturation, followed by phase separation.

6 – Bibliography

1. **UN.** *Globally harmonized system of classification and labeling of chemicals (GHS), 4th edition*. New York and Geneva: United Nations, 2011. www.unece.org. http://www.unece.org/trans/danger/publi/ghs/ghs_rev04/04files_e.html.

2. **IMO.** *MARPOL. Consolidated edition. Unified interpretations of the International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto*. London: IMO, 2011.

3. **GESAMP.** *The Revised GESAMP Hazard Evaluation Procedure*. London: GESAMP, 2002.

4. **REACH.** REACH Regulation (EC) No.1907/2006 concerning Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). *EUR-Lex.europa.eu*. [Online] European Commission, 2006 December 2006. http://old.eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2006R1907:20140410:EN:HTML.

5. **IMO.** *International Maritime Dangerous Goods Code*. London: International Maritime Organization, 2012.

6. **GESAMP.** *Report of the fourth session, GESAMP IV/19*. London: GESAMP, 1972. http://www.gesamp.org/data/gesamp/files/media/Publications/Report_4_Session/gallery_1185/object_1184_large.pdf.

7. —. The evaluation of the hazards of harmful substances carried by ships. Reports and Studies No. 17. London: GESAMP, 1982.

8. —. *The Evaluation of the Hazards of Harmful Substances Carried by Ships. Revision of Reports and Studies No. 17. Reports and Studies No. 35*. London: GESAMP, 1982.

9. *Estimation of the acute inhalation hazards of chemicals based on route-to-route and local end-point extrapolation: experience from bulk maritime transport*. **Hoefer, T., James, D., Syversen, T., and Bowmer, T.** 39(6), s.l.: Altern. Lab. Anim., 2011.

10. **GESAMP.** *Report of the 41st session. Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection, Working Group on the evaluation of the hazards of harmful substances carried by ships.* 2005.

11. **UNCED.** *Declaration on Environment and Development. Agenda 21: Programme of Action for Sustainable Development; The final text of agreements negotiated by Governments at the United Nations Conference on Environment and Development*. s.l.: United Nations, 1992. UN Publications No.E.93.1.11.

12. **IMO.** *International Maritime Solid Bulk Cargoes Code (IMSBC Code)*. London: International Maritime Organization, 2012.

13. —. *International Code for the construction and equipment of ships carrying liquefied gasses in bulk (IGC Code)*. London: International Maritime Organization, 1993.

14. —. *Revised tank cleaning additives guidance note and reporting form*. London: International Maritime Organization, 2007. MEPC.1/Circ.590.

15. —. *Revised Guidelines for the Provisional Assessment of Liquid Substances Transported in Bulk*. London: International Maritime Organization, 2006. MEPC.1/Circ.512.

16. **GESAMP.** *Report of the 32nd Session of GESAMP, GESAMP Reports & Studies No. 73*. London: GESAMP, 2002. http://www.gesamp.org/publications/gesamp-reports-and-studies-71---80.

17. **OECD.** Assessment of Chemicals – Published Assessments. OECD. [Online] *OECD*. http://www.oecd.org/chemicalsafety/risk-assessment/publishedassessments.htm.

18. **European Chemicals Agency (ECHA).** Information on Chemicals. *European Chemicals Agency (ECHA)*. [Online] http://echa.europa.eu/information-on-chemicals;jsessionid=E78DFC4ECA11D79C2E711BE63E9B1192.live2.

19. **EPA, US.** EPA Chemical Safety Research – Methods, Models, Tools and Databases. *US Environmental Protection Agency*. [Online] http://www.epa.gov/research/mmtd/chemsafe.htm.

20. **Japan National Institue of Technology and Evaluation.** Chemical Risk Information Platform. [Online] http://www.safe.nite.go.jp/english/sougou/view/Disclaimer_en.faces.

21. **OECD.** *Principles of Good Laboratory Practice*. Paris: Organisation for Economic Co-operation and Developement (OECD), 1997. ENV/MC/CHEM(98).

22. —. OECD principles for the validation, for regulatory purposes, of (Quantitative) Structure-Activity Relationship Models. *OECD*. [Online] http://www.oecd.org/env/ehs/risk-assessment/37849783.pdf.

23. **US EPA.** US EPA Estimation Program Interface (EPI) Suite for Microsoft Windows, v.4.11. *Exposure Assessment Tools and Models.* [Online] Downloadable software. http://www.epa.gov/opptintr/exposure/pubs/episuite.htm.

24. **IMO.** *International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk with Standards and Guidelines relevant to the Code (IBC Code).* London: International Maritime Organization, 2007. p. 259.

25. **OECD.** *Test Guideline Series No. 305: Bioaccumulation in Fish: Aqueous and Dietary Exposure [Replaces: Bioconcentration: Flow-through Fish Test, 1996].* Paris: Organization for Economic Co-operation and Development, 2012.

26. *Classifying environmental pollutants. Verhaar, H.M.J., C.J. van Leeuwen and J.L.M. Hermens*. s.l.: Chemosphere, 1992, Vols. 25:471-491.

27. **OECD.** *Test Guideline Series No.107: Partition coefficient (n-octanol/water): shake flask method*. Paris: Organization for Economic Co-operation and Development, 1995.

28. —. *Test Guideline Series No. 117: Partition Coefficient (n-octanol/water): HPLC method*. Paris: Organisation for Economic Co-operation and Development, 2004.

29. —. *Test Guideline Series No. 123: Partition Coefficient (n-octanol/water): Slow-Stirring Method*. Paris: Organisation for Economic Co-operation and Development, 2006.

30. *Calculation of drug lipophilicity: the dydrophobic fragmental constant approach, VCH*. **Rekker, R.F.F and R. Mannhold**. s.l.: Verlagsgesellschaft mbH, Weinham, 1992.

31. **Hansch, C. and A. Leo.** *Substituent Constants for Corellation Analysis in Chemistry and Biology*. New York: Wiley Interscience, 1979.

32. *Determination of octanol/water partition coefficeints for hydrophobic organic chemicals with the "slow-stirring" method*. **De Bruijn., F. Busser, W. Seinen and J. Hermens**. s.l.: Environmental Toxicology and Chemistry, 1989, Vols. 8:499-512p.

33. *Generator columns and high pressure liquid chromatography for determining aqueous solubilities and octanol-water partition coefficients of hydrophobic substances*. **De Voe, H., M.M. Miller and S.P. Wasik**. s.l.: J. Res. Natl. Bur. Stand., 1981, Vols. 86 No. 4, 361-366.

34. **Van Leeuwen, C. J., and T.J. Vermeire.** *Risk assessment of chemicals: An introduction*. 2nd edition. Dordrecht: Springer, 2007.

35. **Newsome, L.D., J.V. Nabholz and A. Kim.** Designing Aquatically Safer Chemicals. [book auth.] eds. S.C. DeVito and R.L. Garrett. *Designing Safer Chemicals – Green Chemistry for Pollution Prevention*. s.l.: ACS Symposium Series 640.

36. **ECHA.** *Guidance on the application of the CLP criteria. Guidance to Regulation EC NO 1271/2008 on classification, labelling and packaging (CLP) of substances and mixtures*. Helsinki: s.n., 2012, Vol. Version 3.0.

37. **OECD.** *Test Guideline Series No. 306: Biodegradability in seawater*. Paris: Organisation for Economic Co-operation and Development, 1992.

38. **ECETOC.** *Collation of existing marine biodegradation data and its use in environmental risk assessment*. Brussels: European Centre for Ecotoxicology and Toxicology of Chemicals, 2009.

39. **OECD.** *Test Guideline Series No. 301: Ready Biodegradability*. Paris: Organisation for Economic Co-operation and Development, 1992.

40. **ISO.** *Water quality – Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium – Carbon dioxide evolution test*. Geneva: International Organization for Standardization, 1999. ISO 9439.

41. —. *Water quality – Evaluation in an aqueous medium of the "ultimate" aerobic biodegradibility of organic compounds – Method by analysis of biochemical oxygen demand (closed bottle test)*. Geneva: International Organization for Standardization. ISO 10707.

42. **OECD.** *Test Guideline Series No. 309: Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test*. Paris: Organisation for Economic Co-operation and Development, 2004.

43. —. *Test Guideline Series No. 203: Fish, acute toxicity test*. Paris: Organisation for Economic Co-operation and Development, 1992.

44. **ISO.** *Water quality – Determination of acute lethal toxicity to marine copepods (Copepoda, Crustacea)*. Geneva: International Organization for Standardization. ISO 14669.

45. **US EPA.** *Mysid acute toxicity test, Ecological effects test guidelines*. s.l.: US Environmental Protection Agency, Office of Prevention, Pesticides and Toxics, 1996.

46. **OECD.** *Test Guideline Series No. 202: Daphnia sp. Acute immobilisation Test*. Paris: Organisation for Economic Co-operation and Development, 2004.

47. **ISO.** *Water quality – Marine algal growth inhibition test with Skeletonema costatum and Phaedactylum tricornutum*. Geneva: International Organization for Standardization, 2006. ISO 10253.

48. —. *Water quality – Fresh water algal growth inhibition test with unicellular green algae*. Geneva: International Organization for Standardization, 2012. ISO 8692.

49. **OECD.** *Test Guideline Series No. 201: Freshwater algal and cyanobacteria, growth inhibition test*. Paris: Organisation for Economic Co-operation and Development, 2011.

50. **ISO.** *Water quality – guidance for the preparation and treatment of poorly water-soluble organic compounds for the subsequent evaluation of their biodegradability in an aqueous medium*. Geneva: International Organization for Standardization, 1995. ISO 10634.

51. **ECETOC.** *Aquatic toxicity testing sparingly soluble, volatile and unstable substances*. Brussels: European Centre for Ecotoxicity and Toxicology of Chemicals, 1996. Monograph No. 26.

52. **OECD.** *Guidance document on aquatic toxicity testing of difficult substances and mixtures*. s.l.: Organisation for Economic Co-operation and Development, Paris, 2000. ENV/JM/MONO No.6.

53. —. *Test Guideline Series No. 210: Fish, early-life stage toxicitiy test*. Paris: Organisation for Economic Co-operation and Development, 2013.

54. —. *Test Guideline Series No. 215: Fish, juvenile growth test*. Paris: Organisation for Economic and Co-operation and Development, 2000.

55. —. *Test Guideline Series No. 212: Fish, short term toxicity test on embryo and sac-fry stages*. Paris: Organisation for Economic Co-operation and Development, 1998.

56. —. *Test Guideline Series No. 229: Fish, short term reproduction assay*. Paris: Organisation for Economic Co-operation and Developmenet, 2009.

57. —. *Test Guideline Series No. 230: 21-day fish assay, a short-term screening for oestrogenic and androgenic activity, and aromatase inhibition*. Paris: Organisation for Economic Co-operation and Development, 2009.

58. —. *Test Guideline Series No. 234: Fish, sexual development test*. Paris: Organisation for Economic Co-operation and Development, 2011.

59. **US EPA.** *Pesticides and Toxic Substances, Ecological Effects Test Guidelines OPPTS 850 1350-Mysid Chronic Toxicity Test*. s.l.: United States Environmental Protection Agency, Office of Prevention, 1996. EPA 712-C-120.

60. **ISO.** *Draft Water quality – Calanoid copepod development test with Acartia tonsa*. Geneva: International Organization for Standardization, 2013. ISO 16778.

61. **OECD.** *Series on Testing and Assessment No.79: Validation report of the full life cycle test with the Harpacticoid Copepods Nitrocra spinipes and Amphiascus tenuiremis and the Calanoid Copepod Acartia tonsa – Phase 1*. Paris: Organisation for Economic Co-operation and Development, 2007.

62. —. *Test Guideline Series No. 211: Daphnia magna reproduction test*. Paris: Organisation for Economic Co-operation and Development, 2008.

63. *Use of Health Hazard Criteria for Estimating the Hazard Potential of Chemicals to Water in Case of a Spill*. **Steinhäuser, K.G. and Hofer, T.** s.l.: Regulatory Toxicology and Pharmacology, 2000, Vols. 31: 1-12.

64. **OECD.** *Test Guideline Series No. 420: Acute oral toxicity – fixed dose procedure*. Paris: Organisation for Economic Co-operation and Development, 2002.

65. —. *Test Guideline Series No. 423: Acute oral toxicity – acute toxic class method*. Paris: Organisation for Economic Co-operation and Development, 2002.

66. —. *Test Guideline Series No. 425: Acute oral toxicity: up-and-down procedure*. Paris: Organisation for Economic Co-operation and Development, 2008.

67. —. *Test Guideline Series No. 402: Acute dermal toxicity*. Paris: Organisation for Economic Co-operation and Development, 1987.

68. —. *Test Guideline Series, No. 403: Acute inhalation toxicity*. Paris: Organisation for Economic Co-operation and Development, 2009.

69. —. *Test Guideline Series, No. 436: Acute inhalation toxicity, acute toxic class method*. Paris: Organisation for Economic Co-operation and Development, 2009.

70. *Method for the study of irritancy and toxicity of substances applied topically to the skin and mucus membrane*. **Draize, J.H., G. Woodward and H.O. Calvery.** s.l.: J. Pharmacol. Exp. Ther., 1944, Vols. 82: 377-389.

71. **OECD.** *Test Guideline Series No. 404: Acute dermal irritation/corrosion*. Paris: Organisation for Economic Co-operation and Development, 1992.

72. —. *Test Guideline 430: In Vitro Skin Corrosion: Transcutaneous Electrical Resistance Test (TER)*. Paris: Organisation for Economic Co-operation and Development , 2004.

73. —. *Test Guideline 431: In Vitro Skin Corrosion: Human Skin Model Test*. Paris: Organisation for Economic Co-operation and Development, 2004.

74. —. *Test Guideline 435: In Vitro Membrane Barrier Test Method for Skin Corrosion*. Paris: Organisation for Economic Co-operation and Development, 2006.

75. —. *Test Guideline 439: In Vitro Skin Irritation: Reconstructed Human Epidermis Test Method*. Paris: Organisation for Economic Co-operation and Development, 2010.

76. —. *Test Guideline Series No. 405: Acute eye irritation/corrosion*. Paris: Organisation for Economic Co-operation and Development, 1987.

77. —. *Test Guideline 437: Bovine Corneal Opacity and Permeability Test Method for Identifying Ocular Corrosives and Severe Irritants*. Paris: Organisation for Economic Co-operation and Development, 2009.

78. —. *Test Guideline 438: Isolated Chicken Eye Test Method for Identifying Ocular Corrosives and Severe Irritants*. Paris: Organisation for Economic Co-operation and Development, 2009.

79. **ECETOC.** *Evaluation of Fish Tainting*. Brussels: European Centre for Exotoxicology and Toxicology of Chemicals, 1987. Technical Report No.25.

80. *Establishment of a test guidance for the evaluation of fish tainting*. **Poels, C.L.M., Fischer, R., Fukawa, K., Howgate, P., Maddock, B.G., Persoone, G., Stephenson, R.R., Bontinck, W.J.** s.l.: Chemosphere, 1988, Vols. 17: 751-765.

81. *Impact of Oil and Related Chemicals and Wastes on the Marine Environment*. **GESAMP.** s.l.: IMO, 1993.

82. **ISO.** *Sensory analysis-Methodology-Triangle test*. Geneva: International Organization for Standardization, 1983. ISO 4120.

83. **IMO.** *Guidance on Managing Seafood Safety During and After Oil Spills*. London: International Maritime Organization, 2002.

84. **Whittle, K.J., Anderson, D.A., Mackie, P.R., Moffat, C.F., Shepherd, N.J., McVicar, A.H.** The impact of the BRAER oil on caged salmon. [book auth.] Davies, J.M and G. Topping. *The impact of an oil spill in turbulent waters: the BRAER*. London: The Stationery Office, 1996.

85. **Bonn Agreement.** *Bonn Agreement Counter Pollution Manual*. London: Bonn Agreement, 2005. http://www.bonnagreement.org/eng/html/counter-pollution_manual/welcome.html.

86. **HELCOM.** *Manual on Co-operation in Combating Marine Pollution within the Framework of the Convention on the Protection of the Marine Environment of the Baltic Sea Area 1974 (Helsinki Convention), vol. III: Response to Incidents Involving Chemicals*. Helsinki: Baltic Marine Environment Protection Commission, 1991.

87. **IMO/UNEP.** Regional Information System, Part D, Operational Guides and Technical Manuals. [book auth.] UNEP/IMO. *Practical Guide to Chemical Spills*. s.l.: REMPEC, 1999, updated Jan 2000.

88. **IMO.** Section 1, Problem Assessment and Response Arrangements. *Manual on Chemical Pollution*. London: International Maritime Organization, 1999.

89. *Viscosity extrapolation with temperature*. **Gambill, W.R.** s.l.: Chem. Engineering, 1959, Vols. 127: 123-126.

90. **Lyman, W.J., W.F. Reehl and D.H. Rosenblatt**. *Handbook of chemical estimation methods: Environmental behaviour of organic compounds*. Washington: American Chemical Society, 1990.

91. **OECD.** *Test Guideline Series No. 105: Water Solubility*. Paris: Organisation for Economic Co-operation and Development, 1995.

92. —. *Test Guideline Series, No. 109: Density of liquids and solids*. Paris: Organisation for Economic Co-operation and Development, 2012.

93. **Lide, D.R.** *Handbook of Physics and Chemistry, 82nd edition*. s.l.: CRC Press, 2001.

94. **OECD.** *Test Guideline Series No. 104: Vapour pressure*. Paris: Organisation for Economic Co-operation and Development, 2006.

95. —. *Test Guideline Series No. 114: Viscosity of liquids*. s.l.: Organisation for Economic Co-operation and Development, 2012.

96. **GESAMP.** *Report of the 6th session of the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection*. London: International Maritime Organization, 1974.

97. —. *Report of the 8th session of the Joint Group of Experts on the Scientific Aspects of Marine Pollution. Reports & Studies No. 4*. s.l.: WMO, 1976. http://www.gesamp.org/publications/publicationdisplaypages/report-of-the-4th-session.

98. **OECD.** *Guidance document on aquatic toxicity testing of difficult substances and mixtures*. Paris: Organisation for Economic Co-operation and Development, 2000. ENV/JM/MONO.

99. **Whitehouse, P. and M. Mallett.** *Report No. C – Aquatic toxicity testing for notification of new substances: an advisory document dealing with difficult substances. Report to the chemical notification unit, Department of the Environment (UK)*. Medmenham: Water Research Council, 1993.

100. *Preparation of aqueous media for aquatic toxicity testing oils and oil-based products: a review of the published literature*. **Girling, A.E.** s.l.: Chemosphere , 1989, Vols. 19 (10/11): 1635-1641.

101. *A guideline supplement for determining the aquatic toxicity of poorly water-soluble complex mixtures using water-accommodated fractions*. **Girling, A.E., G.F. Whale and D.M.M. Adema.** s.l.: Chemosphere, 1994, Vols. 29(12): 2645-2649.

102. **CONCAWE.** *Report no. 92/56 – Ecotoxicity testing of petroleum products; test methodology*. Brussels: Conservation of Clean Air and Water in Europe.

Annex I – Terms of reference for the GESAMP EHS Working Group

GESAMP: IMO/FAO/UNESCO IOC/ WMO/WHO/IAEA/UN/ UNEP: Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

UPDATED MEMORANDUM OF 1994

Introduction

1 In the late 1960s, marine pollution problems were of particular concern to several organizations and their subsidiary bodies within the United Nations family. Following consideration by the Administrative Committee on Co-ordination, a number of Agencies agreed in 1967 to establish a joint group of experts to advise them and, as appropriate, through them their Member States, on scientific aspects of marine pollution. In 1993, the sponsoring organizations agreed to extend the role of GESAMP to cover all scientific aspects on the prevention, reduction and control of the degradation of the marine environment to sustain its life support systems, resources and amenities. The Joint Group is open to sponsorship by any organization of the United Nations system concerned wishing to participate in the arrangements described in this memorandum and specifically by, inter alia, supporting the operational costs of the Joint Group. The establishment of this Joint Group was intended, inter alia, to encourage the various organizations concerned at their discretion to disband or to refrain from establishing other interdisciplinary groups on the subject and so to avoid duplication of efforts.

Functions of GESAMP

2 The functions of the Joint Group are:

.1 to provide advice relating to the scientific aspects of marine environmental protection to:

.1.1 the sponsoring organizations on specific questions referred to it;

.1.2 the other organizations of the United Nations system and to Member States of the United Nations organizations on particular problems referred to it through a sponsoring organization; and

.1.3 to prepare periodic reviews and assessments of the state of the marine environment and to identify problems and areas requiring special attention.

3 Such advice is given on the scientific aspects of marine environmental protection, especially those of an interdisciplinary nature, including pollution of the sea as a result of the operation of ships and other equipment in the marine environment; of sea-bed exploration and exploitation; of waste disposal at sea; of discharges of wastes through rivers, land run-off and pipelines; and the pollution of the sea through the atmosphere. The main subject areas on which advice is given include, inter alia:

.1 assessment of the potential effects of marine pollutants;

.2 scientific bases for research and monitoring programmes;

.3 international exchange of scientific information relevant to the assessment and control of marine pollution;

.4 scientific principles for the control and management of marine pollution sources;

.5 scientific bases and criteria relating to legal instruments and other measures for the prevention, control or abatement of marine environmental degradation.

Reports and recommendations

4 The Joint Group reports to the Executive Heads of the sponsoring organizations, which make such reports available to Governments and, as appropriate, to other international organizations, institutions and individuals concerned with marine pollution problems. Each sponsoring organization arranges for distribution of these reports according to its own needs.

5 Any recommendation by the Joint Group which pertains to or requires for its implementation concerted action by several of the sponsoring organizations may be referred to relevant ACC subsidiary bodies.

6 Proposals and recommendations relevant to the work of other organizations which are not among the sponsors of the Joint Group are, as appropriate, communicated to such organizations.

Membership

7 Each sponsoring organization nominates from one to four experts according to their needs. The Joint Group is composed of such nominees, the experts being appointed to act in their individual capacities. The multidisciplinary composition of the Joint Group is agreed among the sponsoring organizations. Some experts are nominated to serve for a period of up to four years to provide a continuing nucleus, while others can be appointed as occasion demands, having in mind the particular subjects to be considered at each session of the Joint Group.

Participation in sessions

8 Sessions are normally held annually and in rotation at the headquarters of the sponsoring organizations. In certain circumstances however the Joint Group may be convened elsewhere.

9 Organizations of the United Nations systems which are not among the sponsors of the Joint Group may be represented at its sessions. Other organizations which are not members of the United Nations systems may also be invited to send observers to sessions of the Group by agreement among the sponsoring organizations.

Financial arrangements for sessions

10 The sponsoring organizations share appropriately the costs of conference services and documentation pertaining to sessions of the Joint Group. Each sponsoring organization accepts responsibility for the expenses for participation in sessions by the experts it nominates and for maintaining contact with such experts.

Secretariat

11 IMO acts as the Administrative Secretariat for the Joint Group and assigns the Administrative Secretary; each sponsoring organization assigns a Technical Secretary. The Administrative and Technical Secretaries form a joint secretariat. The Administrative Secretary maintains continuity and keeps the central archives relative to the work of the Joint Group. The Technical Secretary from the organization hosting a session acts in each case as the secretary for the session and takes responsibility for the preparation of the report of that session. The provisional agenda for each session is drawn up jointly by the sponsoring organizations under the initiative of the Administrative Secretary and after consultation with the Chairman, taking into account any suggestions received from any organizations in the United Nations system which may be interested in taking part in the session.

Procedure of work

12 Detailed arrangements for the conduct of the business of the Joint Group and for its support (including inter-secretariat preparations, intersessional activities, sharing of responsibilities for documentation, costs of sessions, election of officers, conduct of sessions, routing of correspondence, etc.) are covered by guidelines based on this memorandum and drawn up jointly by the Secretaries.

GESAMP Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships (GESAMP EHS)

The terms of reference of the GESAMP EHS Working Group, as given by GESAMP at its 6th session in Geneva (1974) (96) and amended at its 8th session in Rome (1976) (97) are:

> *"To examine and evaluate data and to provide such other advice as may be requested, particularly by IMO, for evaluating the environmental hazards of harmful substances carried by ships, in accordance with the rationale approved by GESAMP for this purpose".*

These terms of reference remain unchanged.

Annex II – Members of the GESAMP EHS Working Group

This list represents past and present members of the GESAMP EHS Working Group. Those marked with an asterisk have served as Chairman of the Group.

Ms D.M.M. Adema	Netherlands
Dr O. Awodele	Nigeria
Dr B. Ballantyne	United States
Dr F. Bathie	United Kingdom
Dr B-E. Bengtson	Sweden
Dr R. Blackman	United Kingdom
Dr C.T. Bowmer*	Netherlands
Mr D. Enreth	United States
Prof W. Ernst*	Germany
Mr L. Foyn	Norway
Dr T. Höfer	Germany
Mr P. Howgate	United Kingdom
Dr D. James	United Kingdom
Dr P. Jeffery*	United Kingdom
Dr W. Jiang	China
Dr R. Kantin	France
Dr M. Kitano	Japan
Dr S. le Floch	France
Dr P. Lefcourt	United States
M R. Luit	Netherlands
Dr M. Marchand	France
Dr S. Micallef	Malta
Mr M. Morrissette	United States
Prof. S.D. Murphy	United States
Dr F. Pedersen	Denmark

Dr J.K. Portmann*	United Kindom
Dr P.H. Rodriguez	Chile
Dr H. Saito	Japan
Prof T. Syversen	Norway
Dr G.H. Thompson	United States
Prof. E. Vigliani	Italy
Dr M. Wakabayashi	Japan
Mr T.A. Wastler	United States
Dr P. Wells*	Canada
Dr K.W. Wilson	United States
Prof. T. Yoshida	Japan
Dr V. Zitko	Canada

Secretariat to the EHS Working Group – Past and present

Mr S.L.D. Young	Secretary	1974-1976
Mr B. Okamura	Secretary	1977, 1993
Dr M. Nauke	Secretary	1978-2000
Mr J.V.C.Crayford	Secretary	2001-2004
Dr S. Micallef	Secretary	2005-2007
Dr K. McDonald	Secretary/Technical Advisor	2008-2014
Ms P. Charlebois	Secretary	2013-2014
Dr P. Jeffery	Technical Advisor	1989-1992
Mr N. Soutar	Technical Advisor	1993-2013

Meetings of the EHS Working Group

1	14–15 October	1974	London	28	15–19 February	1993	London
2	4–6 June	1975	London	29	14–18 February	1994	London
3	15–17 October	1975	London	30	27 February–3 March	1995	London
4	12–14 July	1976	London	31	28 August–1 Sept	1995	London
5	22–24 October	1976	London	32	20–24 May	1996	London
6	9–13 May	1977	Delft	33	10–14 February	1997	London
7	4–6 July	1977	London	34	23–27 February	1998	London
8	22–26 May	1978	Bergen	35	1–5 February	1999	London
9	5–9 November	1979	Burnham	36	3–7 April	2000	London
10	2–6 June	1980	London	37	31 April–4 May	2001	London
11	15–19 December	1980	Houston	37a	6–10 August (toxicologists)	2001	London
12	21–25 September	1981	London	37b	5–9 November (ecotoxicologists)	2001	Tokyo
13	25–29 October	1982	Delft	37c	18-19 April (phys-chem experts)	2002	Brest
14	6–10 June	1983	London	38	22–26 April	2002	London
15	9–13 January	1984	Aberdeen	39	5–9 May	2003	London
16	21–25 May	1984	London	40	19–23 April	2004	London
17	11–15 February	1985	Plymouth	41	9–13 May	2005	London
	7–11 October	1985	London	42	20–24 February	2006	London
18	26–30 May	1986	Delft	43	6–8 June	2006	London
19	3–7 November	1986	London	44	30 April–4 May	2007	London
20	18–22 May	1987	Trondheim	45	22–25 April	2008	London
22	18–22 January	1988	London	46	20–24 April	2009	London
23	29 August–2 Sept	1988	London	47	26–30 July	2010	London
24	13–17 February	1989	London	48	11–15 April	2011	London
25	26–30 March	1990	London	49	25–28 June	2012	London
26	8–12 April	1991	London	50	15–19 April	2013	London
27	17–21 February	1992	London	51	12-16 May	2014	Brest

Annex III – System for assigning chemical names

Both GESAMP and the IMO bodies responsible for the pollution categorization of substances are required to consider the name of each substance, in order to ensure that it is:

- unique;
- properly defines the composition of the substance or mixture;
- properly reflects the associated hazards; and is
- preferably self-explanatory.

The EHS Working Group of GESAMP examines the nomenclature of each substance submitted and assigns a chemical name. Accepted rules of chemical nomenclature are generally applied, while avoiding excessively complicated or long names. Bearing in mind that many chemicals are in fact proprietary mixtures or preparations and provided the four points above can be met, the EHS Working Group is generally amenable to using names which make clear to which chemical group the substance belongs, without divulging its exact chemical structure in the interests of confidentiality. To ensure a proper hazard evaluation by th EHS Working Group, knowledge of the full chemical structure is essential. Trade names are not accepted.

The EHS Working Group provides the manufacturer with a hazard profile and proposes a working name for the substance. When the manufacturer submits the name and hazard profile plus additional (largely safety related) data to the appropriate IMO bodies, in order to allow categorization, a "proper shipping" name is then assigned by IMO. While generally similar to names given by GESAMP, the proper shipping name may be simplified for everyday use and easy recognition, as well as to reflect relevant safety concerns on board ship.

The definitions of substances and mixtures used here are those given in the GHS.

Mixtures (complex)

The length of hydrocarbon chains is of importance in assessing the hazard of complex mixtures, e.g. the number of carbon atoms and the molecular weight greatly influence aquatic toxicity. With the alkanes, aquatic toxicity increases from C5 (pentane, the first liquid homologue) to C9, the most toxic.

Thereafter, acute aquatic toxicity decreases and disappears, as solubility in water decreases below concentrations sufficient to cause an effect in short-term tests.

Mixtures (isomeric)

Isomeric mixtures are generally indicated with the word (all isomers) in brackets after the name. Where one isomer is more hazardous than the rest, then the worst case rating(s) in the hazard profile is assigned. Less hazardous isomers may be named separately, reflecting their appropriate hazards.

Mixtures (containing a particular component)

Natural mixtures are generally named so as to identify their composition and to prevent any other substances (with different hazards) being carried under the same name. Where a given component can affect the hazard profile by its presence, it is usually specified, e.g. "resin acids <10%".

Mixtures (preparations)

Deliberate mixtures, e.g. formulations or preparations, are generally named so as to reflect all the most important components, particularly where the quantity of one component may influence the hazard of the whole mixture, e.g. Alkyl acrylate/vinyl pyridine copolymer in toluene. In this case, if the mixture has not been tested with the toluene component present, then toluene will be evaluated and the most severe profile of the two applied.

Mixtures (solutions)

Solutions always refer to aqueous solutions unless otherwise specified. Usually, the strength of the solution is specified after the name if the concentration indicates a relevant hazard limit. Where the word "solution" is given after the name of a substance without specifying the strength of that solution, then the hazard profile applies to all strengths, i.e. the ratings for human health and environmental properties are the same for all strengths. Alternatively, the strength of solution may be given by the manufacturer to indicate the maximum practicable or safe concentration that may be carried in water. Solutions are defined as mixtures under the GHS.

Mixtures (molecular weight)

Sometimes the molecular weight (range) is cited in brackets after the name. This is done for several reasons:

- where the molecular weight of all the components is >1000, the substance is unlikely to bioaccumulate or exert aquatic toxicity (the molecules are too big to pass through cell membranes);

- substances may be produced in several molecular weight ranges with varying hazard profiles and the molecular weight may be conveniently used to separate them.

Mixtures (polymeric chains)

The length of polymeric chains is indicated by the prefix "poly" followed by the number of units in brackets, then by the name of the monomeric unit.

Pesticides

Pesticides have been given an ISO name for the sake of clarity (and brevity) and this is indicated by including (ISO) in brackets after the name.

Physical state

Where a substance is normally a solid, it may be transported in bulk by heating, in which case, the word "molten" appears in brackets after the name.

Annex IV – Biodegradation tests suitable for testing under marine conditions

Table IV.1 – *OECD biodegradation tests specifically developed for testing under marine conditions*

Guideline	Name	Principle of the method	Scope and recommended usage
OECD No. 306 (1996) [31]	Marine biodegradation test 1. Shake flast method 2. Closed bottle method (seawater variant of the closed bottle test OECD 301)	Method using natural seawater as the aqueous phase and the sole source of microorganisms (i.e. an innoculum is not added as in freshwater tests) to evaluate the biodegradability. Suitable for lower test substance concentrations. In a more conservative test, DOC removal or ThOD are measured in a 28d closed bottle test (can also be extended to 56d).	The test can be used for organic substances which: • are soluble at the test concentration (Shake flask method, 5 to 40 mg/l DOC; Closed bottle, 2 to 10 mgl-1 DOC); and • are volatile providing suitable precautions are taken. Relatively simple test method suitable for measuring the ultimate biodegradation of organic chemicals in seawater. Despite the use of natural seawater bacteria, this is not a simulation test owing to the addition of nutrients.
OECD No. 301 E (1992) [33]	Shake flask method (seawater variant of the modified screening test)	Suitable for higher test substance concentrations. DOC removal or ThOD are measured in a shake flask test lasting for up to 60d.	Idem ditto
OECD No. 309 (2004) [36] Based on ISO/ DIS 14592-1 (see below) and elements from OECD 307[12] and 308[13]	Aerobic mineralization in surface water – Simulation biodegradation test	Simulation test to measure the time course of biodegradation and kinetic rate of a test substance at low concentration in aerobic natural water (fresh, brackish or marine): a) shake flask batch test b) semi-continuous operation for long test times, in order to prevent deterioration of the test microcosm.	Suitable for testing substances at very low concentrations (<1 µg/l to 100 µg/l) to ensure that the biodegradation kinetics reflect those expected in the environment, that the test substance will serve only as a secondary substrate, that the biodegradation kinetics is expected to be first order ("non-growth" kinetics) and that the test substance may be degraded by "cometabolism". The use of ^{14}C labelled test substances and the determination of the phase distribution of ^{14}C at the end of the test, enable ultimate biodegradability to be determined.

Table IV.2 – *ISO biodegradation simulation design, specifically developed for testing natural (fresh) water*

Guideline	Name	Principle of the method	Scope and recommended usage
ISO 14592.1 [93] **ASTM E-1279** **EPA-OPPT** **S 835-3170; refers to test type 1 only**	Shake flask batch test Water quality evaluation of the aerobic biodegradability of organic substances at low concentrations in water. Method follows the die-away of the parent compound.	Method for evaluating the biodegradability of organic substances at low concentrations by aerobic microorganisms in water. • Part 1 is designed to simulate surface water or sediment-water suspensions, while Part 2 is a continuous-flow simulation of a river, including biomass attached to surfaces. • Evaluation of the test result is carried out by specific chemical analysis of the parent compound. • Part 1 uses stoppered flasks with an air headspace, while Part 2 uses an open cascade type system.	The test can be used for organic substances which are water soluble at the test concentration (preferably <100µg/l); this includes many poorly soluble substances. The test method is suitable for measuring the primary biodegradation of substances at environmentally realistic concentrations.

[12] OECD 307, Aerobic and anaerobic transformation in soils

[13] OECD 308, Aerobic and anaerobic transformation in aquatic sediment systems

Annex V – Aquatic toxicity tests with poorly soluble complex mixtures

1 Introduction

Aquatic toxicity tests should be based on dissolved exposure concentrations; most modern test guidelines provide instructions to this effect. However, with poorly soluble mixtures, this is often difficult if not impossible to determine with any degree of certainty due to the differential solubility of the various components. Typical examples of such chemicals are hydrocarbon distillates in general, and more specifically "lubricating oil additives". This standard operating procedure was developed in the 1980s to replace traditional dispersion tests for measuring aquatic toxicity, where the undissolved test material was often found to cause physical effects on the test organisms.

Several documents have been published which provide guidance on testing difficult substances in general. The most informative of these is that published by ECETOC, which provides a step-by-step practical key to selecting the appropriate dosing and exposure techniques to match the expected behaviour of the test substance in water. Of probably more regulatory importance, is an OECD guidance document on "aquatic toxicity testing of difficult substances and mixtures" (98), which describes a wide variety of differing test conditions. It focuses on the definition of "exposure concentrations" and the provision of supporting analytical evidence and provides some guidance on when it is appropriate to use water accommodated fraction techniques such as the one described below.

The method described here was originally designed for use in the preparation of test media for aquatic toxicity testing of hydrocarbon mixtures. However, it is suitable for the preparation of other poorly soluble complex mixtures in seawater. Generally, the method follows the recommendations for testing difficult substances provided by Whitehouse and Mallet (99) and uses "water accommodated fractions" (WAF). It is based on methods developed by Girling (100) and Girling et al. (101) and adopted by CONCAWE (102).

2 Terminology and definitions

- The term **test substance** is used here to describe mixtures, whether simple or complex, and includes both natural mixtures, such as oils and isomeric mixtures from a chemical process, as well as artificial or deliberate mixtures such as preparations.
- The term **water accommodated fraction** (WAF) refers exclusively to mixtures and is not applicable to pure substances (equivalent term: aqueous extracts).
- Although it contains a dissolved substance, a WAF can best be referred to in reporting as the **test medium** and not as the "test solution".
- The initial concentrations mixed in seawater should be consistently referred to as the **loading rate** when presenting results and not as the "test concentration", as the initial amount was never present in the media actually tested.

3 Principles

3.1 The test substance is first homogenized thoroughly, bearing in mind that mixtures with a tendency to emulsify in water may have to be rolled or shaken for several hours and then weighed out immediately.

3.2 As a WAF should ideally comprise a differential equilibrium of the components of the mixture, between the non-dissolved and the dissolved phases, each test concentration/loading rate of a series must be prepared separately. Dilution of a single stock is not acceptable.

3.3 If it is uncertain how long the major components of the substance will take to reach equilibrium with the water phase, then a preliminary study should be run, samples should be taken after, e.g. 4, 16 and 20 hours stirring and analysed with an appropriate analytical method.

3.4 Accurately weighed amounts of homogeneous test substance are thoroughly mixed with a given volume of (sea)water using a magnetic stirrer, i.e. for a period that is long enough to obtain an equilibrium between the (sea) water and the test substance. The mixture is then left to stand for a further short period, to allow for phase separation. It is desirable to confirm that equilibrium has been reached by chemical analysis of relevant components or other suitable means, e.g. total organic carbon (TOC).

3.5 Following phase separation, the required volume of test medium is tapped off from the middle of the mixing vessel. Substances may float, settle to the bottom or remain in suspension, depending on their specific gravity. This "clear" fraction is called the "water accommodated fraction" (WAF). The WAF may contain very small (invisible) droplets or particles.

3.6 The WAF is used directly for testing except in cases where it is judged to be sufficiently turbid as to cause physical hampering of the test organisms (particularly crustaceans). In such cases, it may be filtered through a glass wool plug. In order to prevent losses of sparingly soluble substances by evaporation (filtration under low pressure) or adsorption (in filter material), the WAF may not be filtered through a fine membrane or other filter. Centrifugation may be considered, if no other alternatives are available.

3.7 Substances containing volatile components may have to be mixed and tested in sealed vessels. Substances that degrade rapidly may need shorter equilibrium and shorter phase separation times.

4 Apparatus

Ordinary laboratory apparatus is used, in particular:

- magnetic stirring apparatus
- glass stoppered Erlenmeyer flasks with a glass tap assembly appromixately 3 cm above the base
- laboratory balance
- glass microscope cover slips
- time clock(s) for electrical power (if possible)

5 Preparation of the test media

Start the preparation of the media one day (20 h + 4 h) in advance of the test exposure.

5.1 Homogenize the test substance thoroughly, e.g. by rolling overnight on a roller bank in a cool environment (15°C to 20°C).

5.2 Accurately weigh the necessary amounts of test substance. Small amounts may be weighed on a glass microscope cover slip (one amount for each test solution to be prepared); avoid the use of non-inert materials to transfer the test substance.

5.3 Fill Erlenmeyer flasks (with a glass stopper) almost completely with a known amount of seawater (the seawater type and temperature of choice for the test). Introduce a suitable teflon/glass magnetic stirring rod and place each of these flasks on a magnetic stirrer at about the test temperature, making sure that the vortex reaches a depth of ⅓ of the water column. The depth of the vortex is important in ensuring that the individual loading rates are stirred with approximately equal energy.

5.4 Introduce the weighed amounts of test substance, one for each flask, when the seawater is already stirring; this may improve the mixing procedure.

5.5 The preparation of the WAFs is generally carried out in the dark as some substances, e.g. hydrocarbons, may be sensitive to photo-oxidation.

5.6 Stir for 16–20 h, followed by 4 h standing for phase separation. If possible, carry out the stirring a few degrees below the test temperature, as stirring may slightly warm the seawater.

5.7 Following the period allowed for phase separation, tap the WAFs from the middle of the water column directly into the test vessels (not more than 70% of the volume).

5.8 This procedure is followed on each occasion the test media are replaced, i.e. for a 96 h (fish) test with daily renewal, the test media are prepared 4 times.

6 Reporting

Refer accurately to the procedure in the report:

- state that water accommodated fractions were used;
- give the stirring and standing times;
- quote the results as lethal loading rates and effect loading rates (LL_{50}, EL_{50}, NOEL) etc., not as LC/EC_{50}s or NOECs.

Annex VI – GESAMP EHS Product Data Reporting Form

Please note that this form may be amended from time to time. The most up to date form may always be accessed at the following URL under the heading 'related documents' on the right hand side of the page:

http://www.imo.org/ourwork/environment/pollutionprevention/chemicalpollution/pages/chemicalsreportingforms.aspx

GESAMP
Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

GESAMP/EHS Product Data Reporting Form

Characteristics of Liquid Chemicals Propose for Marine Transport

Section 1 – Product Identity

Proper Shipping Name*	
Main Chemical Name	
Main Trade Name	
Synonyms	

*This is the first name that should appear on the shipping documentation and will be reflected in the IBC Code

Section 2 – Product Identification Numbers

CAS Number	
EHS Number	
UN Number	

Section 3 – Product Chemical Details

Chemical Formula:	
Physical State During Transport: (liquid, solution (with %) or molten)	
Chemical Structure:	

Section 4 – Composition

Component name	%	Range	Type

GESAMP/EHS Product Data Reporting Form

Section 5 – Physical Properties

Property		Qual	Value or Range	References and Comments
Molecular Weight				
Density @ 20ºC	**(kg/m^3)**			
Flash Point (cc)	**(°C)**			
Boiling Point	**(°C)**			
Melting Point/Pour Point	**(°C)**			
Water solubility @ 20ºC	**(mg/l)**			
Viscosity @ 20ºC	**(mPa.s)**			
Vapour Pressure @ 20ºC	**(Pa)**			
SVC @ 20ºC	**(mg/l)**			

Notes:

1. If values are not available at 20ºC temperature, please provide the value and reference temperature.
2. SVC refers to saturated vapour concentration. This value is used to assess the inhalation hazard for products that may be toxic by inhalation, but may not produce vapours in sufficient concentrations to constitute an inhalation hazard.

Section 6 – Relevant Chemical Properties

Water Reactivity (0 – 2) [ ]

0 Any chemical which, in contact with water, would not undergo a reaction to justify a value of 1 or 2.

1 Any chemical which, in contact with water, may generate heat or produce a non-toxic, non-flammable or non-corrosive gas.

2 Any chemical which, in contact with water, may produce a toxic, flammable or corrosive gas or aerosol.

Details/References [ ]

Does the product react with air to cause a potentially hazardous situation? (**Y/N)** [ ]

If so, provide details [ ]

Reference [ ]

Is an Inhibitor or Stabilizer needed to prevent a hazardous reaction? (Y/N) [ ]

If so, provide details [ ]

Reference [ ]

Is refrigeration needed to prevent a hazardous reaction? (Y/N) [ ]

If so, provide details [ ]

Reference [ ]

GESAMP/EHS Product Data Reporting Form

Section 7 – Mammalian Toxicity

7.1 Acute Toxicity

		Qual	Value or Range	Species	Reference/ Comments
Oral ATE/LD_{50}	(mg/kg)				
Dermal ATE/LD_{50}	(mg/kg)				
Inhalation ATE/LC_{50}	(mg/l/4h)				

7.2 Corrosivity and Irritation

	Observation	Species	Reference/Comments
Skin Irritation/Corrosion*			
Eye Irritation			
* If corrosive, exposure time (hrs)			

Options: not irritating, mildly irritating, irritating, severely irritating or corrosive

7.3 Sensitization

	Y/N	Reference/Comments
Respiratory Sensitizer (in humans)		
Skin Sensitizer		

7.4 Other Specific Long-term Effects

	Y/N	Reference/Comments
Carcinogenic		
Mutagenic		
Toxic to reproduction		
Other long-term effects		

7.5 Relevant Mammalian Toxicity

Acute Mammalian Oral Toxicity Data Taken Into Account

Effect	Qual	Value or Range	Units	Species	Reference

GESAMP/EHS Product Data Reporting Form

Acute Mammalian Dermal Toxicity Data Taken Into Account

Effect	Qual	Value or Range	Units	Species	Reference

Acute Mammalian Inhalation Toxicity Data Taken Into Account

Effect	Qual	Value or Range	Units	Species	Reference

Skin Irritation/Corrosion Data

Qty (mg)	Cover	Exp. Time (hrs)	Species	Observation	Reference

Eye Irritation Data

Qty (mg)	Cover	Exp. Time (hrs)	Species	Observation	Reference

Additional Notes on Mammalian Toxicity

Section 8 – Aquatic Toxicity, Bioaccumulation and Biodegradation

8.1 Acute Toxicity

	Units	Qual	Value or Range	Species	Reference
Fish LC_{50}	mg/l/96h				
Crustacea EC_{50}	mg/l/48h				
Algae IC_{50}	mg/l/72h				

8.2 Chronic Toxicity

	Units	Qual	Value or Range	Species	Reference
Fish LC_{50}	mg/l/96h				
Crustacea EC_{50}	mg/l/48h				
Algae IC_{50}	mg/l/72h				

8.3 Biodegradation and Bioaccumulation

Test	Units (%)	Qual	Value	Method
28d Biodegradation				
BOD_5				
COD				
BCF				
Log Pow				
Reference				

8.4 Acute Fish Toxicity Taken Into Account

Effect	Qual	Value or Range	Units	Species	Reference

8.5 Acute Crustacea Toxicity Taken Into Account

Effect	Qual	Value or range	Units	Species	Reference

8.6 Acute Algal Toxicity Taken Into Account

Effect	Qual	Value or Range	Units	Species	Reference

8.7 Bioaccumulation – BCF values

Qual	Value or Range	Duration (days)	Species	Reference

8.8 Bioaccumulation – Log Pow Values

Qual	Value or Range	Duration (days)	Species	Reference

8.9 Biodegradation Values

Qual	Value or Range	Duration (days)	Species	Reference

8.10 Additional Aquatic Toxicity Notes

8.11 Additional Bioaccumulation Notes

8.12 Additional Biodegradation Notes

The Revised GESAMP hazard evaluation procedure

Columns A and B Aquatic environment					
	A Bioaccumulation and Biodegradation			B Aquatic Toxicity	
Numerical Rating	A1 Bioaccumulation		A2 Biodegradation	B1 Acute Toxicity	B2 Chronic Toxicity
	log Pow	BCF		LC/EC/IC50 (mg/l)	NOEC (mg/l)
0	<1 or > ca.7	no measurable BCF	R: readily biodegradable	>1000	>1
1	≥1 – <2	≥1 – <10	NR: not readily biodegradable	>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 – < ca.7	>4000		>0.01 – ≤0.1	
6				≤0.01	

Columns C and D Human health (toxic effects to mammals)						
	C Acute Mammalian Toxicity			D Irritation, Corrosion and Long-term health effects		
Numerical Rating	C1 Oral Toxicity LD_{50}/ATE (mg/kg)	C2 Dermal Toxicity LD_{50}/ATE (mg/kg)	C3 Inhalation Toxicity LC_{50}/ATE (mg/l)	D1 Skin irritation and corrosion	D2 Eye irritation and corrosion	D3 Long-term health effects
0	>2000	>2000	>20	not irritating	not irritating	**C** – Carcinogenic
1	>300 – ≤2000	>1000 – ≤2000	>10 – ≤20	mildly irritating	mildly irritating	**M** – Mutagenic **R** – Reprotoxic
2	>50 – ≤300	>200 – ≤1000	>2 – ≤10	irritating	irritating	**Ss** – Sensitizing to skin **Sr** – Sensitizing to respiratory system
3	>5 – ≤50	>50 – ≤200	>0.5 – ≤2	severely irritating or corrosive **3A** Corr. (≤4 h) **3B** Corr. (≤1 h) **3C** Corr. (≤3 min)	severely irritating	**A** – Aspiration hazard **T** – Target Organ Toxicity **N** – Neurotoxic **I** – Immunotoxic
4	≤5	≤50	≤0.5			

Column E Interference with other uses of the sea			
E1 Tainting*	E2 Physical effects on wildlife and benthic habitats	Numerical rating	E3 Interference with Coastal Amenities
NT: not tainting (tested)	**Fp:** Persistent Floater	0	no interference ***no warning***
T: tainting test positive	**F:** Floater	1	slightly objectionable ***warning, no closure of amenity***
	S: Sinking Substances	2	moderately objectionable ***possible closure of amenity***
		3	highly objectionable ***closure of amenity***

* Tainting has been deleted as a regulatory criterion for classifying substances. Substances that have already been rated on this basis continue to be listed in sub-column E1 in the GESAMP Composite List.

Science for Sustainable Oceans

ISSN 1020–4873