Interspill 2015
WHITE PAPER

Cargo information needed during the initial stages of a chemical spill

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Summary

Based on practical experience, the type of information needed during the initial stages of a spill and sources for such information is discussed. How the information provided in the GESAMP Hazard Profile may assist is explained, particularly when cargo information is limited. The new guidance document for hazard assessment by GESAMP is presented in order to demonstrate its potential use during maritime emergencies. The multi-stakeholder approach in carrying out the evaluations and generating the hazard profiles is explained. Based on styrene as an example, we show how practical experiments validated the scientific assessment by GESAMP. The limitations of the Hazard Profile when used under emergency conditions will also be identified.

Introduction

Upon receipt of an emergency call from a chemical tanker in distress, a notification of a spillage originating from a ship, or a loss of containers containing chemicals, one of the first tasks facing the maritime emergency command or first responders is to look for cargo hazard information. In such situations, there is an urgent need for reliable information on the behavior of the product and potential hazards to crew, ship and the environment, as well as to the responders entering the scene.
The information requirements discussed here are those which are required during the first phase of the incident, in the initial hours following a release. In this period a basic set of data is needed. During later stages of the emergency operations, more sophisticated information is needed. In the more advanced stages of the response, additional experts will be involved, in particular those with more detailed expertise on the products concerned and those with additional practical knowledge and on-scene experience.

Information types and sources

Initial product information may come from many sources, such as the ship manifest, the ship management company, or the product manufacturer. However, experience has shown that cargo information is often not readily available on board the ship or from the ship management company and may take some time to access . Upon request, the systems established by the chemical industry to obtain reliable information during an emergency, such as safety data sheets for such products or similar products, can be accessed. For example, the cooperation in Europe between the governmental bodies responsible for maritime emergencies, the European Maritime Safety Agency (EMSA) and the chemical industry is well established. The Intervention in Chemical Transport Emergencies (ICE) is a co-operative programme, set up by the European chemical industry to achieve this goal. A specialized cooperation had been created for maritime emergencies as the MAR-ICE network together with EMSA and with CEDRE as the focal point providing a framework for effective assistance and co-operation in the event of a chemical incident at sea between partnering countries within the EU.

If more detailed information is needed during an incident, it is up to the maritime emergency command to get into contact with national administrations to obtain additional information on the cargo, which could be available for chemical products that had gone through approval procedures (as for example consumer products or biocides) or which had been presented for licensing chemical factories or tank farms. Within the European Union confidential data are available via poison control centers in case of human exposure.

However, even if this information is available, specific assessment of the properties for determining the behavior of the cargo in the marine environment is generally not included. It is then up to maritime emergency managers to call in scientists and ask them for an immediate evaluation of the specific product data in order to assess the behavior of a given product in the environment. The means of integrating scientific experts into an emergency situation may differ. If scientists are not working within the command structure, they may be requested from governmental scientific institutions or from the chemical industry´s co-operative programmes.

In a number of cases, during exercises as well as during emergencies, responders did not get a correct picture of the cargo's behavior, i.e. whether the cargo would evaporate, float, dilute or sink after spillage. However, this is important information and is essential for salvage operations. There are sophisticated vessels that have the capability of collecting floating liquids. However, if the cargo has evaporating or sinking properties, or the cargo dilutes very well in sea water, such vessels are of no use at all. On the other hand, an evaporator may create a hazard for the responders if the substance is toxic by inhalation or flammable. For significantly poisonous evaporators, personal respiratory equipment is needed and the use of traditional response equipment such as helicopters and conventional coast guard vessels will be limited.

In addition to the chemical behavior, the human toxicity of a bulk liquid is critical for assessing the risk to those involved in the operations. It is therefore essential to obtain credible information on the acute inhalation toxicity of the cargo. In addition, it is important that potential hazards created by aerosols also be considered. Leakages from holds and pipes containing liquids under pressure, spilled liquids under wave action and vapors in foggy or wet climate may create aerosols of the liquid cargo.

It is important to obtain all information on the health hazards associated with the cargo. There have been cases where responders were not sufficiently protected against products that were corrosive to the skin or which could generate long-term health hazards, such as carcinogenicity (e.g. epichlorohydrin). On the other hand, the collection of floating non-toxic and non-corrosive liquids from the sea surface allows for the option of using specialized oil recovery vessels.

In the case of a spill, assessing the toxicity of the bulk liquid to aquatic life is of secondary importance. Once released into the environment, the chemical will normally be diluted (assuming it has significant solubility) and it's impact on aquatic life will be based on its concentration in the sea. In maritime emergencies, there is no realistic possibility for collecting a chemical once it is diluted in the water. The information on aquatic toxicity is of value for overall environmental risk assessment and risk communication to the public. For a tanker involved in an accident, it is also important to be aware of the potential hazards of cargoes carried in undamaged tanks should the tanker seek a port of refuge. The acceptance of a damaged tanker will strongly depend on the risk to the local environment.

Information concerning the bioaccumulation of chemicals in aquatic organisms and its biodegradation potential is important for estimating the impact of a substance on local fisheries, coastal aquaculture and for identifying the long-term effects of the spill. It will be important for post-spill monitoring and for assessing the damage claims against the polluter, potentially under the HNS Convention (when in force), in the aftermath of the spill.

The GESAMP information

Today, the most reliable summary of the hazards associated with bulk liquids, as just explained, is immediately available from the GESAMP Hazard Profile for a substance, published by the IMO. The hazard profile is composed of ratings showing the toxicity and the physical characteristics that create the hazards, which will be outlined later in detail.

The GESAMP Hazard Profiles are established by the Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships (GESAMP/EHS), a specialized working group of the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP). GESAMP is a scientific advisory body composed of 10 organizations of the United Nations that have responsibilities in respect to the marine environment or the use of the oceans, e.g. the International Maritime Organization (IMO), the Food and Agriculture Organization (FAO) and the United Nations (UN) itself with its Division of Ocean Affairs and the Law of the Sea, among others.

GESAMP/EHS is composed of an international group of scientists that come together to evaluate the hazards of liquids transported in bulk by ship. Some 1800 products are listed as potential liquid cargoes for the world tanker fleet. Every year GESAMP/EHS, through the IMO, updates its list of some 900 chemicals, with associated GESAMP Hazard Profiles, based on the assessments carried out by the GESAMP/EHS. These assessments are carried out based on the criteria set out in the “The Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships”. The background and history of this work had already been outlined at a workshop at INTERSPILL 2009 in Marseille (Hoefer 2009). Since then, more and more regional emergency response centers are aware of this information and using the hazard ratings derived from these assessments, based on the scientific evaluation of data provided by the manufacturer, available in open scientific literature or in databases used by the GESAMP experts.

The 2nd edition of the evaluation guideline including, in particular, amended sections on the behavior of chemicals in the sea, has just been published (GESAMP 2014). The most up-to-date hazard profiles developed during expert meetings are published every year on the IMO website as the “composite list of hazard profiles” (http://www.imo.org/OurWork/Environment/PollutionPrevention/ChemicalPollution/Pages/ChemicalsReportingForms.aspx).

GESAMP categorizes the hazard ratings under five headings: (A) bioaccumulation and biodegradation, (B) aquatic toxicity, (C) acute mammalian toxicity, (D) irritation, corrosion and long-term health effects, and (E) interference with other uses of the sea.

Section A - bioaccumulation and biodegradation

The potential of bioaccumulation in marine organisms is shown in ratings representing rising steps of a factor of 10. From a practical standpoint, ratings of 4 and 5 in column A1 are indicating a significant effect which may led to long-term existence of residues in marine organisms.
The biodegradation is orientated on the real potential of the marine environment to degrade the spilled substance. A rating of NR in column A2 clearly indicate that a significant biodegradation is not be expected in the marine water.

Section B - aquatic toxicity

The toxic effect on marine organisms, like fish, crustaceans and algae, is shown in ratings that represent a tenfold increase in toxicity. Depending on the dilution after spillage, experts can extrapolate the potential effects on the local marine population. The acute effects (within days) and the chronic effects (within weeks) are shown in the separate ratings of B1 and B2.

Section C - acute mammalian toxicity

The evaluated chemical's lethal effect to humans is rated in three columns, C1, C2 and C3, representing its toxicity by ingestion, skin contact and inhalation. The values presented are based on doses and concentrations representing a 50% chance of death by exposure. The severe but non-lethal poisoning will require less exposure. In general, ratings of 2 to 4 identify chemicals which are regulated and labelled as toxic with a skull and crossbones label internationally.

Section D: irritation, corrosion and long-term health effects

The scales for skin and eye irritation under columns D1 and D2 are harmonized, with a rating of 2 reflecting potential irritation that will ebb away , whereas a rating of 3 indicates a substance that may destroy skin or eye tissue.
The long-term health hazards are shown in letters in column D3, which are explained in the GESAMP guidance. A rating of C representing carcinogenicity is the most relevant for practical occupational health protection on scene. The generally non-lethal but specific target organ toxicity effect is given a T rating in column D3.

Section E: Interference with other uses of the sea

The behavior of a spilled chemical in water and air is shown in column E2. The European Behavior Classification system provides a set of criteria for evaluating the short-term distribution between water and air which has been fully integrated into the GESAMP assessment. This system is well known by all concerned parties that are involved in the handling of HNS spillages at sea. The primary behavioral classifications are identified as sinkers (S), dissolvers (D), floaters (F), evaporators (E), and gases (G). Based on practical experience and regulatory requirements, GESAMP has added a category for persistent floaters (Fp) for substances with high viscosity such as mineral oil fractions that will result in water surface oiling and/or beach oiling.
Another sophisticated rating system is shown in column E3. This rating considers the behavior of a spilled chemical as well as the hazard to humans due to toxicity, corrosivity or flammability and proposes warnings and exclusion or evacuation zones on beaches, following a spill. These ratings could also be used in the case of unprotected vessels approaching a spill area.

The ratings in column E3 are based on worst-case scenarios. The classifications in column E2 likewise “give a worst case rating” according to the guideline. The rating provided is a guide only; 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 experts before a decision is taken.

Behavior classification and the real world

In October 2000 the chemical tanker *Ievoli Sun*, carrying styrene as its main cargo, was in distress in the English Channel due to severe weather conditions. French maritime authorities responded to the distress call and emergency operations started. In this incident, the GESAMP classification and the European Behavior Classification (as shown in column E2 of the GESAMP Hazard Profile) for styrene were consulted to identify possible hazards and behavior. The situation was further complicated when the vessel sank. Whilst monitoring the area, styrene was detected as a slick on the water surface, in some marine organisms and in the air. Styrene vapors were also detected some distance away, due to its strong odor (see detailed report by Le Floch 2009). The distribution of the chemical vapours corresponded only partly with the behavior classification as FE, identifying styrene as a floater and evaporator.

Given the observations, it was believed that part of the spilled styrene had been diluted in the sea. The most important indication was the chemical analysis of seafood from the surrounding area. Based on the FE classification for styrene, significant concentrations of styrene in the water phase would not normally be expected. As such, styrene appeared to be a good starting point to initiate validation experiments for the European Behavior Classification system.

The experiments at sea were designed and performed near Brest (France) by CEDRE scientists, in consultation with GESAMP experts. The details of these experiments have been published (Fuhrer et al 2012). For the purposes of the experiment, styrene was spilled within floating cells on the sea. Further to this, measurements were taken to identify traces of styrene in the water phase, at the surface and in the air. These measurement parameters were consistent with the classifications for diluters (D), floaters (F or Fp), and evaporators (E). Of course, there are some differences between the experimental design and what would occure in a real spill in open waters. However, the simulation was designed to be similar to the circumstances encountered during an emergency.

Immediately after the styrene was released, its spread on the sea surface was observed resulting in floating slicks. Approximately half of the floating substance was lost during the initial 4.5 hours, either transformed into the water phase or evaporating in the air. From the data generated, it was assumed that about 50% of the styrene spilled was diluted in the water column and remained there for at least several hours. According to the measurements taken in deeper waters, a significant portion of the styrene was diluted in the ocean. It was assumed that the water turbulence at the surface had introduced energy allowing for the transfer of more styrene into the water than had occurred using standardized laboratory methods for measuring the water solubility of styrene. In a calmer environment, with less stirring energy, a lower fraction of the spilled material might dilute in the water phase. The experiments indicated that the evaporation of styrene in real scenarios might be far lower than expected based on the theoretical extrapolations according to the European Behavior Classification system. It was concluded that under ordinary marine conditions, the classification of styrene as a floater and evaporator could be misleading for the purposes of risk assessment. However, the situation could be different in calm weather with no significant wave energy. Related results were optained for Xylene (also classified as FE) in similar experiments (Le Floch et al 2011; Le Floch 2012). Xylene slicks on the water surface were relatively transient, emulsified and the dissolution process became dominant.

The GESAMP ratings should therefore be understood as information to be used for calm weather conditions. With more turbulent waters and significant waves, many floaters, sinkers and evaporators will also distribute in the water column. However, for marine incidents the ratings in columns E2 and E3 of the GESAMP hazard rating system provide useful information for the assessment and response decisions related the protection of personnel and the deployment of vessels, helicopters and personnel for on-scene response.

When comparing the experimental outcome and the accidental spillage in the *Ievoli Sun* incident, the E3 rating of 3, the most severe rating indicating closure of beaches developed by GESAMP-EHS - equivalent to hazards for crews on vessels near the spill – was a realistic model rather than erring on the precautionary side as the hazards produced a real risk for crews and bystanders. It was concluded that, for such cases, a simple model was the best and most practical way of providing basic information for the initial response actions to be taken for a maritime spill.

Discussion

While GESAMP hazard profiles are established for international regulatory purposes under the auspices of IMO, they can nevertheless provide immediate critical information to assist first responders in assessing the hazard of a particular chemical substance and mount an appropriate response. Further to the establishment of the GESAMP hazard profiles, which identify hazards and physical (behavior) properties, IMO bodies use these profiles for assigning appropriate carriage requirements for the transport of bulk liquids in chemical tankers. While these simple numerical and letter-based ratings can be used in a more or less direct manner in a regulatory application, their use in maritime emergencies requires appropriate background knowledge on the hazard assessment and rating procedure in order to interpret the ratings and make response decisions accordingly. It is therefore essential that experts within maritime emergency command structures understand the basic principles by which the ratings were developed. Up to now, there have been no requests for a more simplified version of the published GESAMP procedure or for a version of the ratings that could be easily understood by laymen in the field of scientific hazard assessment.

When discussing the use of the GESAMP Hazard Profile within the German scientific expert group that advises the German Central Command for Maritime Emergencies, some shortcomings were identified. The most important information needed at the initial stages of an incident is to determine the possible flammability of the cargo, which is not covered anywhere in the GESAMP Hazard Profile. Information regarding chemical reactivity and explosivity is also needed, but these parameters are equally not evaluated by GESAMP in any way. For the long-term perspective, information about the chemical and physical degradation would be value-added to the information already presented for biodegradation.

The advice given by GESAMP on potential limitations on the use of beaches and the seaside is taken into consideration by national administrations, e.g. in Germany. However, these ratings are based on worst case scenarios. Therefore, additional factors related to the spill situation, such as weather, hydrodynamic conditions, etc., must be evaluated by competent spill responders. However, no practical guidance in this respect is yet available.

GESAMP Hazard Profiles are only available for about 900 chemicals (substances, mixtures and generic entries), about the same number of products (IMO 2014) are allowed to be shipped globally as covered by the international regulatory framework for the transport of bulk liquid chemicals, established by IMO. Simulation exercises and an actual incident in Europe have demonstrated the practical consequences of the limits of using hazard profiles in a maritime incident. However, the profiles provide useful information for first responders and it should be noted that all large volume bulk liquids have been assigned GESAMP hazard profiles.

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