HNS DETECTION AND MONITORING

RECENT INCIDENTS AND FUTURE CONSIDERATIONS

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Source: French Navy

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Introduction

The volume of chemicals (HNS) transported by sea is increasing leading to an increased risk of accidents. A Hazardous and Noxious Substance is a term used to describe a substance other than oil which, if introduced into the marine environment is likely 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.

Marine pollution caused by HNS differs from oil pollution in having a much wider range of potential fate and behavior once released into the marine environment. The selection of the appropriate response options to an HNS incident requires detailed knowledge of the involved substance's physical and chemical properties. In fact, before starting any detection or monitoring operation it is important to have an idea of what could happen with the substance in relation to its chemical properties. The European Behavior Classification system (SEBC code), established by the European Union, provides a set of criteria for evaluating the short-term behavior of chemicals spilled at sea. With this information, then it is possible to define a detection and monitoring plan well adapted to the event's geographic location and that location's particular atmospheric, sea surface, water column and/or sea bottom 'compartments' and characteristics. This paper presentation examines the topic largely on the basis of experiences acquired in recent incidents in which *Cedre* (Centre of Documentation, Research and Experimentation on Accidental Water Pollution) was involved; namely the *Levoli Sun*, the *Ece* and the *Princess of the Stars*.

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In October of 2000, the *Levoli Sun*, a chemical tanker, sank in the Channel carrying an estimated 4000 tons of Styrene, 1025 tons of Methyl-Ethyl-Keton (MEK), and 1000 tons Isopropyl Alcohol (IPA).

In order to determine the impact these chemicals would have, the GESAMP classification and SEBC code were consulted. The GESAMP classification was used to assess the impact in the marine environment associated with the chemical of concern, whereas the EBC code was used to predict the behavior of the substance.

The GESAMP classification is based on the GESAMP hazard evaluation procedure which provides a range of information on the properties of substances with respect to the protection of the aquatic environment and human health (GESAMP, 2002). The Hazard Evaluation Procedure generates a final chemical ranking, which in turn determines the assigned pollution category. For liquid bulk chemicals, there are four pollution categories (X, Y, Z and Other Substances).

The SEBC code concerns only the short-term behavior of chemicals. This code is based on their physicochemical properties, which are pre-defined in a laboratory using normalized conditions and procedures. Five primary behavioral categories are identified as Gas (G), Evaporates (E), Floaters (F), Dissolvers (D) and Sinkers (S), with combinations being represented as GD, ED, FED, etc.

In the *Ievoli Sun* context, information gathered pertaining to the classifications described above indicated that the spilled products of concern were known to exhibit three distinctly different behavioral characteristics. Styrene is a toxic substance and a relatively insoluble compound; Methyl Ethyl Ketone (MEK) is considered to have a low-toxicity impact and is relatively soluble; while Isopropyl Alcohol (IPA) is deemed to have no toxic effects and is highly soluble.

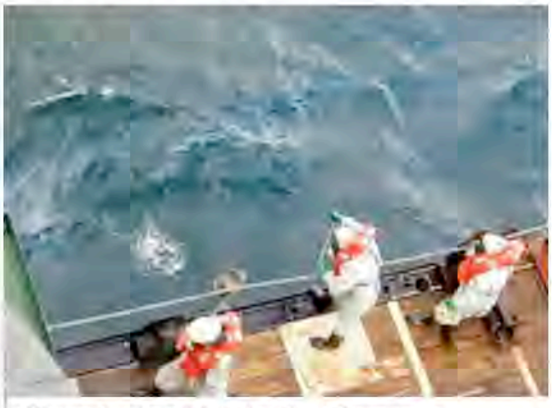

Figure 1 – Ievoli Sun Incident Response

As for monitoring of the event, at the time of the incident, the French Navy observed leakage of Styrene using a submersible drone, and IFREMER (French Marine Research Institute) detected Styrene in the gills and tissue of crabs caught in the vicinity of the wreck by fishermen. Initially visual surface observations showed a Styrene 'slick' (see Figure 1) on the surface. Furthermore, styrene vapors were detected at nearby Alderney Island both through odor detection and GC-MS samples, but were never detected as such on the French shoreline. Over time additional attempts were made to detect Styrene by means of direct water sampling, however this was ineffectual, probably due to high-intensity currents that resulted in significant dilution (or 'spreading') of the Styrene.

The current detection of Styrene in water requires a large sample volume. Field sampling is unwieldy and is not very realistic. And for water column testing, the inability to detect styrene concentrations calls for a new method of detection altogether, which could replicate successful laboratory methodologies. For example several in-situ sensors would be useful for the purpose of monitoring on-site at strategic locations. Also, rather than focusing on just collecting sample concentrations, the development of equipment which is able to project the chemicals behavior in the water column is necessary. This will allow for strategic planning for both the regions of concern and for chemicals with similar characteristics. As an example of this, Cedre developed an experimental column ("Cedre Experimental Column") which allows prediction of the solubility of a chemical product in seawater during its transfer. This prediction is an attempt to satisfy the basic need of estimating the volume of the cargo, which will reach the sea surface. Also, standards for biological markers and bio-monitoring tools would enable decision makers to better determine the impact of a spill. Bio-monitoring programs, based on caging techniques, or others techniques such as Semipermeable Membrane Devices (SPMD), could be of interest to evaluate the potential bio-accumulation of a particular compound and, by extension, their bio-magnification.

Concerning the Styrene slick at the sea surface, its detection and the monitoring of its drift were rather difficult, and no information was obtained about its size. For products such as Styrene, colorless but altering light reflection by changing sea surface state ("rugosity"), and visual observations, remains to date the most suitable, albeit difficult, option. There is a lack of known data concerning product detectability using available sensor technology such as UV-Fluorometers. New development of these types of sensors could improve both response as well as assessment.

In response to toxic clouds, like the one produced at this spill, the civil security authorities had no other choice than to install a network of vehicles to monitor Styrene in air on the western coastline of Manche Department (Figure 2). This was more of a pretense or display of response and monitoring, as opposed to a real preventive action. Had the Styrene been detected in the air, it would already have been quite late to make the decision to confine the potentially effected nearby population within their homes or to order the evacuation of people in danger of intoxication. Measurements such as the clouds drift, size, and concentration would have been helpful for response and safety. This would have enabled responders on site to notify local communities about the approaching chemical cloud. Also, further study needs to be done in order to determine the behavior of the volatilized product.

Figure 2: Vehicle of the French civil security authorities deployed for air monitoring.

Ece

The *Ece*, another chemical tanker, sank in the Channel with a cargo of Phosphoric Acid. This chemical (and like chemicals) have a higher density than water. As such the spill remained near to the sea floor. This made it difficult to monitor and follow the plume. The major concern with the release of the acid was its interaction with the sea floor, and its ability to kill organisms in the immediate area, as well as to potentially release heavy metals that likely would have collected on the sea floor. Furthermore, the innate equilibrium of phosphoric acid in seawater may lead to an increase in phosphate species, potentially resulting in algal blooms.

What made this response particularly problematic was the difficulty in obtaining water column samples near the sea floor. Also, current sampling techniques are unable to detect Phosphate directly in seawater. These difficulties point to the need for new technologies and methods for detecting these types of spills both in the water column and within sedimentary/seafloor samples.

Princess of the Stars

The *Princess of the Stars*, a ferry-boat, sank in a storm in the Philippines. In this incident, one of the most significant difficulties was the fact that no information concerning environmental parameters was available on the area. Even once the predicted behaviour of compounds was established, it was extremely difficult to make informed decisions in order to target the optimum sampling points. This was particularly problematic given the high-dissolution rate of the product, which compounded the difficulty of determining which direction the chemical-compounds would spread and would they be nearer to the sea floor, or higher up in the water column? This difficulty again underlines the fact that response, detection and monitoring plans need to be defined, accounting for basic information regarding the cargo as well as the local environment. Furthermore, the need for rapid data collection in remote areas is absolutely necessary for better response.

There seems to be a clear and present need for the development of adequate sensors to provide the capabilities to detect low concentration of various HNS in the sea, their drift within the sea and at sea surface, as well as models to predict their behavior and patterns in air. Conscious of these needs, Cedre and InterOcean Systems have begun to cooperate to investigate the adaptation of existing sensors used for oil spill and petrochemical spill detection and monitoring, for utilization also with HNS-types of chemicals and compounds. Any successes in this regard would likely advance both the tracking of oil slicks, and chemicals, in the sense that detecting individual components of oil would inherently help in analyzing the weathering and evaporation of substances such as crude oil. In the future, oil behavior at sea could be better understood by analyzing any and all of these components.

Spill Detection and Monitoring Overview

The use of new technologies can play a critical role in prevention, early response, and monitoring of oil and chemical spills. There are numerous technologies available for both remote and in-situ monitoring, which may be used for both point-source and non-point source applications.

The following summarizes a number of available technologies and techniques that offer potential solutions: Spectrometry, Fluorometry, UV and IR Absorption, Optical and Thermal Imaging/Cameras, Particle Size Analysis, Radio Frequency Absorption, Radar (i.e. FLIR, SAR, SLAR, LIDAR, HF), and others. This is not an exhaustive list, but points to the availability of sensing methodologies that warrant consideration and in some cases further development for operational use in the field of spill prevention, monitoring and response.

While many of these sensor technologies are primarily used at present for oil spill prevention and response, it is the authors' belief that many of these technologies could be adapted for use in suitable HNS-classified chemical spill prevention and response applications. Each of these sensing/sampling methods has differing attributes, and strengths and weaknesses, and each offers relative merit depending on the application and situational variables such as chemical pollutant type, physical/chemical characteristics, operating platform, environmental conditions, activity purpose (i.e. early-detection, monitoring, response, clean-up, remediation), etc.

For wide area surveillance of surface/near-surface oil spills, remote satellite imagery, air-borne imaging systems and vessel-borne radar are currently used successfully as a tool for oil spill monitoring and response. These may be useful as well with respect to monitoring and response of HNS chemical spills. And likewise there are a number of other in-situ, point-source and hand-held/portable sensors used for hydrocarbon spills that may be readily adaptable for use with various chemical spills.

UV Sensor Technology for Hydrocarbons

As an example, the fixed-mounted UV (Ultraviolet) filter-fluorometer, pictured in Figure 3, is commonly used for early warning detection of hydrocarbons by entities such as marine terminals, refineries, industrial plants and others to monitor at effluent outfall points. It may also be used for early warning detection of hydrocarbons to protect desalination plant intakes, mariculture/fish farms, and sensitive habitats such as wetlands, which are particularly vulnerable to the incursion of oil spills (and other types of pollution spills).

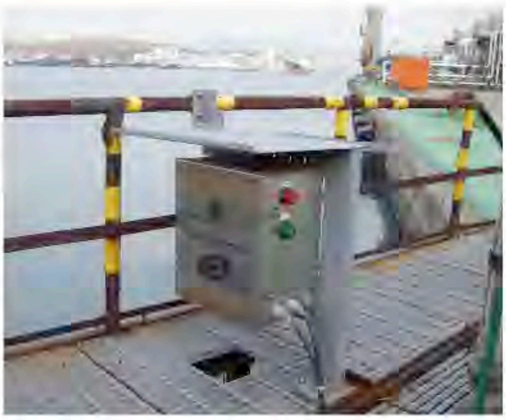

Figure 3 – Terminal/Pier Oil-Sensor & Alarm

This particular sensor was developed specifically for the detection of a wide range of hydrocarbons, including crude oil, heavy fuel oils, turbine oil, lubricants, diesel, jet fuel, and a long list of PAH and BTEX types of compounds. It is a non-contact optical sensor proven to be a very effective as a tool for real-time detection; enabling automated containment, and/or early warning alarm and response - which prevents 'worse-case' scenarios from happening and minimizes cleanup costs and environmental damages.

This sensor detects the presence of oil by using UV excitation and then measuring the difference between light absorbed versus light emitted. Oils are known to fluoresce, thus this optical property allows for the reliable detection of hydrocarbons (PAHs and BTEX) using this methodology. For example, hydrocarbons typically absorb light between 300-400nm, and emit light in the longer 450 to 650nm range.

At present this type of sensor is used principally for real time point source monitoring of oil spill events, for example (as mentioned) at effluent outfalls, water intakes, and as a strategically placed protective event-alarm 'barriers' around sensitive/protected habitats and environments. However, the sensors' inherent adaptability for installation in varied environments (in-shore, industrial settings, piers, harbors, coastal and offshore), a couple of which are depicted in Figures 4 and 5, suggests that this technology could be adapted for applications well beyond its current uses.

Figure 4 – Offshore Loading Buoy with Sensor & Alarm

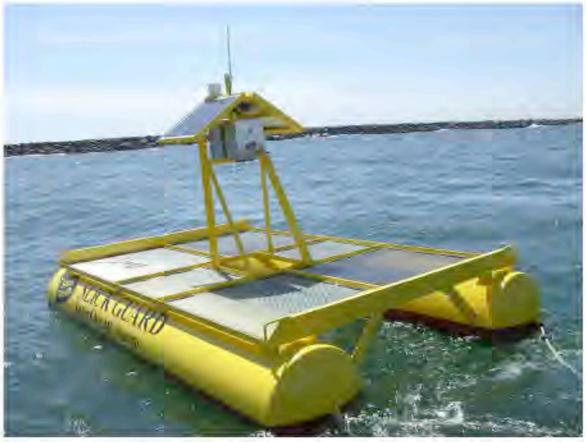

Figure 5 – "Slick guard" Buoyancy Platform Environmental Sensor System

UV and Other Sensor Technology for HNS (Non-Hydrocarbons)

In the course of experimentation with this particular UV-type sensor, it has been determined that it can be tailored for additional applications, and in some cases for detection and monitoring of a wider range of chemical compounds such as HNS types of chemicals. For example this same hydrocarbon sensor can also be used to detect many types of food oils, molasses, Glycols (which are water soluble), and many other substances that may similarly warrant detection but have yet to be properly tested in the lab and in the field. This provides an example of an existing technology that could be adapted for many useful purposes.

Further investigation could be instructive for how this and other existing technologies could be useful in prevention, monitoring and response scenarios. For example, continuing with the example of this particular UV sensor; it could be used for detection and monitoring of Styrene and/or Palm Oil (see Figures 1 and 6), both of which were the focus of recent spill incidents. Figure 7 shows the relative fluorescence of various hydrocarbons using UV excitation. This chemical response characterization could be greatly expanded and documented to include many additional HNS chemicals.

Figure 6 – Alegra Incident Response

Conclusion

As a course of further study, research and development, the database of all HNS chemicals and standard response techniques could be expanded to include the physical and behavioral properties of each substance, together with a description of which types of sensor technologies can be used for detection and monitoring in any given environment and / or response scenario. Of course there are, and would be, many unknowns in putting together a comprehensive list such as this. However, over time, and through experimentation and field experience, the database / knowledge-base would become an instructive and useful resource, greatly improving prevention, response and monitoring capabilities as they pertain to many HNS substances of concern.

Figure 7 – Relative fluorescence of various hydrocarbons

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