KISH P & I LOSS PREVENTION CIRCULAR KPI-LP-13-2012
(Selected Spill Incidents & Lessons to be Learnt)

The following notes contain 26 selected & documented spill incidents, identified by type of cargoes on board the case-ships, with the main lessons learnt in relation to the type of pollutant or chemical concerned.

CASE STUDIES :

Group A) Containers and packages

Five incidents involving container ships are analysed here:

1- Case1, 1997, wrecked in high seas off Azores, Portugal, loss of 74 containers, one with radioactive cells.

2- Case2, 1997, 20° list in the English Channel, with 70 t of HNS onboard.

3- Case3, 2001, Brittany, Molène Island, France, stranded with 218 containers and 330 cases.

4- Case4, 2006, stranded south of Ré Island with, among other cargo, containers of cocoa beans.

5- Case5, 2007, the English Channel, structural failure with 600 containers on board.

A1) Case1:

In 1997, the container carrier Case1, sailing off the coast of Azores in a violent storm, broke in two. The 34 crew members were safely evacuated. Seventy four containers of beverages, flammable and combustive products, marine pollutants and corrosive substances were lost. The aft part of the ship was taken in tow while the fore part sank at a depth of 3000 m. During towing, it appeared that the ship had one container onboard containing 3 biological irradiators, with their radioactive sources (Cesium 137).

Research indicated that the container transporting the biological irradiators was positioned in the sunken part of the ship. The protective cells of the radioactive sources were designed to resist a pressure of 20 atmospheres. Thus, they imploded while at a depth of some 200 m when the half ship was sinking. The French Institute of Protection and Nuclear Security (IPSN) carried out assessments of the possible impacts on the fauna in the vicinity of the wreck and on bottom fish consumers. The great depth (3000 m), the high dilution and the absence of fisheries in the area limited the exposure risk.

A2) Case2:

In 1997, inadequate tank ballasting in the container ship in the bay of Seine, led to a 30° list of the vessel off Cherbourg. The ship was beached by the salvors in a shallow bay. A study of loading plan indicated the presence in containers of approximately 70 t of dangerous substances, in particular flammable gases and liquids, as well as corrosive and oxidizing substances. The ship also contained 2900 t of fuel oil. The 32 crew members were evacuated and taken to hospital. The risk of pollution of the marine environment required not only full cargo information, but also direct observation of the state of the ship and its cargo and dialogue with experts of the shipowner. Finally, the hold contents were pumped out; the ship recovered its normal waterline, and was towed at high tide to Cherbourg harbour.

A3) Case3:

In 2001, the container ship Case3 missed the Ushant traffic separation scheme by 17 miles and ran aground at full speed on a sandy beach of the island of Molène. It carried 218 containers and 330 cases on board, loaded with 1078 t of various goods (tobacco, alcohol, telephones, honey, glycerine, metals, furniture, cigars, catalyst, empty packaging). The catalyst, 17 t in one container, was classified IMDG class 9. The ship also had 180 t of fuel oil and 60 t of diesel oil on board. The ship was refloated at high tide and towed to a waiting area in the Bay of Berthaume for inspection by French Navy divers before being towed to dry docks, following verification of the actual hazards associated with the catalyst. Enlargements of a poor quality photocopy allowed identification of the shipper of the product, a Mexican company in Ciudad Del Carmen. It indicated its phone number and qualified the product as "mezcla quimica" (chemical mix). After waiting for the office to open in Mexico, learned that the shipment was the return of a rejected French product with nothing more dangerous in its composition than diesel oil as a solvent. Shortly thereafter, the convoy was allowed to enter the Bay of Brest and the dry dock.

On the following day, fuel began to leak from a breach to the ballast tanks under the ship, indicating that the internal partitions of the double bottom were damaged and that fuel had circulated between the fuel and ballast tanks. The pumping operations to completely clean the ship before repair and the cleaning of the dry dock extended over several days. The duration of these operations, carried out under optimal conditions, in a confined space, showed the damage that Molène Island had escaped. Had the ship not been refloated immediately, it would have been gradually dismantled by the winter storm, requiring cleaning operations extending over several months.

A4) Case4:

On 24 October 2006, at 4 a.m., the container ship Case4, faced with an engine failure in a storm, was stranded by winds, currents and waves on a submerged rocky bank, one nautical mile south of Ré Island. The ship had on board, amongst other cargo, containers of cocoa beans, wood and least 500 t of fuel oil (IFO 380) and 50 t of marine diesel. The crew was airlifted to safety, except the Master and 5 crew members that remained to assist the salvors with the response measures.

The ship had a breach in the hull and listed at a 20° angle. No pollution was observed, but the marine pollution response plan of Charente Maritime was activated nevertheless. The high seas oil spill response vessel Case4 sailed from Brest with containment and recovery equipment. The first investigations showed that it was impossible to refloat the vessel at high tide that evening. The following day, divers detected a 20 m long breach, confirming that it would be impossible to tow the vessel in her current state.

The Préfecture de département decided to protect the oyster beds in the area using booms. Two barges equipped with skimmers and with storage capacity were deployed. On 30 October, 430 m³ of fuel was pumped out of the tanks and stored on the Case4. The main concern then turned to the 300 containers of cocoa beans onboard the vessel.

By the third day of immersion, a great abundance of suspended matter and turbidity was observed in the water. Over time, an increasing proportion of beans sank and a white oily film on the surface indicated the release of lipids. Monitoring of the gaseous release showed the generation of hydrogen sulphide by the fermentation of cocoa beans in seawater. The "préfet maritime" of the Atlantic issued an order to the shipowner to remove the wreck and its cargo. Removal of the containers and the cargo of timber began on 10 November 2006. The speed of operations was dictated by the sea state. Several openings were made in the vessel to access the various decks and to remove the cargo trapped within. Together with the salvage plan, a pollution contingency plan was established, which consisted of

deploying a boom around the entire site and pre positioning oil recovery equipment (skimmers, sorbents, booms, etc.). On 9 March 2007, the salvage company began to remove the wreck's superstructures.
The cutting up and removal of the superstructures continued until September 2007. The hull could not be refloated. It was cut into five vertical sections, which were removed by a crane barge, prior final disposal at a demolition site. The last section of hull was hoisted out of the Port of La Pallice on 28 November 2007. Residual debris was removed and the works were finalized on 19 December.

A5) Case5:
On 18 January 2007, the British container ship the Case5 en route from Antwerp to Lisbon, was caught in a storm at the entry to the Channel. She suffered a leak and a failure of her steering system. She was transporting 2394 containers, carrying nearly 42000 t of merchandise, of which some 1700 t were classed as hazardous substances (explosives, flammable gases, liquids and solids, oxidants, toxic substances, corrosive materials...). In her bunkers, she held over 3000 t of heavy fuel oil. The 26 crew members were evacuated from the vessel by rescue helicopters. The French Préfecture Maritime of the Atlantic conducted a risk assessment before carrying out a towing attempt on the abandoned ship. Drift predictions was carried out in the case of a spill and analysing the pollution risks posed by products in the cargo classed as hazardous, selected from a 106 page list containing up to 7 entries per page.
Two types of dangers were examined, and discussed: the risks for responders *(explosive or flammable substances and toxic gases)* and the risks for the marine environment (aquatic pollutants, toxic substances for the flora and fauna). The difficulty in this type of situation was not so much the dangers caused by a single product in isolation, for which information could be found in specialised technical literature, but rather the possibility of interference and reactivity between the products. Despite these uncertainties, the risk analysis was carried out in six hours and by midnight a committee of experts had finalized the hazard assessment, having provided a detailed opinion to the operational services of the "maritime prefect".
The risk of the vessel breaking during towing could not be excluded. Following inspection, the assessment team gave clearance for the Case5 to be towed and the decision was made to head for Portland, on the Dorset coast.
Whilst en route, due to the growing risk of the vessel breaking, the convoy was diverted to Lyme Bay, where the Case5 was beached.

In total, 103 containers were lost overboard, with 57 of the containers being washed ashore, many on Branscombe beach. The cargo of motorcycles, wine casks, nappies, perfume, car parts etc. attracted hundreds of scavengers, despite police warnings that any wreck material recovered must be reported.
In France, packets of chocolate biscuits, made in Turkey and covered in fuel oil, landed on the northern Finistère and Côtes d'Armor coasts over the weekend of the 27 28 January 2008. Questions were raised as to whether the packets of biscuits and the fuel oil came from the Case5.
Backtrack drift modelling showed that this was possible. Samples of the Case5 fuel oil were compared with samples collected on the shoreline. While analysis was underway, the Turkish manufacturer of the chocolate biscuits was identified on the Internet and contacted. The company provided the references of two containers loaded with 14 t of the biscuits (200000 packets). These were the two containers lost overboard at the beginning of the incident. There was no doubt left.

Over the following week, local communities from Finistère and Côtes d'Armor, helped by a Civil Protection Response Unit, cleaned up sandy beaches and rocky areas polluted by accumulations of oiled biscuit packets and patches of fuel oil.
In Lyme Bay, the shipowner unloaded the containers and the fuel from the ship. By the end of March, all the containers on the deck and the fuel oil had been unloaded. An assessment made at this stage indicated that it would not be possible to refloat the vessel with its cargo onboard and a decision was made to remove all the remaining containers. The first phase of the removal of the Case5 could then begin. In August 2008, the bow section was towed to a yard in Northern Ireland. The stern section was expected to follow by mid 2009. Biomonitoring, carried out by the University of Plymouth, was implemented in the bay to assess the general impact of the incident and the particular impact of ship's bunker oil.

Lessons Learnt :
i) Faced with a world of extreme diversity, with the initial concerns of the responders were to identify the exact location of the containers in/on the ship and the specific product contained in each container, but also to gather information on product packaging. This information was sought in order to determine whether the container/package would either float or sink if were to fall overboard and to what extent the packaging included a waterproof layer.
ii) As a consequence of the high diversity of the chemicals present on the vessel, responders had to identify and quantify both the individual fate of each chemical, as well as the possible reactions resulting from the mixing of two or more substances.
iii) The great majority of chemicals involved in the incident had only a temporary and localized impact on marine life. No impact studies were implemented following the cleaning operations.

Group B) Packages / Containers on fire
Two incidents involving packages and/or containers catching fire are analysed hereunder:
1-Case6, 1985, Somalia, stranded and on fire with 118 containers of hazardous chemicals (acetone, butyl acetate, tetraethyl lead, toluene, trichlorethylene, xylene).
2-Case7, 1987, cape Finisterre, Spain, 22 chemical products and fuel oil representing 1000 t of chemicals, almost 5000 barrels, cans, containers or bags of flammable products (xylene, butanol, butyl acrylate, cyclohexanone, sodium),toxic products (aniline, diphenyl-methane, O cresol, dibutyl phthalate) and corrosive products (phosphoric acid, phtalic anhydride).

B1) Case6:
While sailing out of the Port of Mogadishu (Somalia), the container ship Case6 grounded on rocks approximately 100 m from the shore. She was transporting a cargo of 118 containers of hazardous chemicals, including acetone, butyl acetate, tetraethyl lead, toluene, trichloroethylene and xylene.

Attempts for her salvage failed. As time passed, she continued to list. Part of the deck collapsed and a fire started above one of the decks. Toxic fumes and chemical emissions drifted towards the city. Authorities ordered the evacuation of a number of inhabitants and companies in the port area. The vessel broke in two and large quantities of oil and cargo, including drums of chemicals, began coming ashore. A few days later, the rear part of the ship broke off and the vessel began to list at 90 degree angle. Despite the lack of protective clothing, an operation was initiated to recover the cargo washed up on the shore.

B2) Case7:

While sailing off the coast of Spanish Finisterre, in December 1987, the general cargo vessel Case7 announced a fire on board and requested assistance. The fire spread and the ship lost control. In spite of fast deployment of the rescuers, 23 of the 31 crew members died. Towing attempts failed, the fire propagated, the ship drifted and ran aground on rocks only 100 m from the coast, near the town of Corcubion.

The hull was damaged and water penetrated the holds. It was only after grounding that the full diversity of the cargo became known. Part of the cargo on deck was being unloaded (orthocresol and formaldehyde), when a series of explosions occurred. Operations were suspended. The complete declaration of the loading list disclosed the presence of close to 1000 t of chemicals onboard, including 1400 barrels of sodium and 10 containers of flammable, toxic and/or corrosive chemicals loaded on deck. There were 300 barrels of butanol (D, MARPOL CAT , cat Z), O cresol (MARPOL CAT , cat Y), cyclohexane (E, MARPOL CAT , cat Y), aniline (MARPOL cat), butacrylate (FED, MARPOL CAT , cat Y) and phtalic anhydride (MARPOL CAT , cat Y) bags in the five cargo holds. Fifteen thousand people within a 5 km radius were evacuated overnight. Once the danger of explosion was ruled out, quality control of air, water and marine organisms was carried out. The results showed moderate levels of air and water contamination. Continuing bad weather conditions facilitated the dispersion and neutralisation of the chemicals spilled. Analyses of marine organisms (mussels, barnacles, octopuses) showed no bio accumulation of aniline nor orthocresol.

Lessons Learnt :

i) The difficulty of responding to a fire on a vessel that is transporting a variety of toxic products.

ii) The importance of having quick access to public or private means and personnel for responding in a toxic environment.

iii) The difficulty of rapidly obtaining a fully detailed list of the products transported and the loading plan, in order to properly assess the dangers for response personnel and the public.

iv) That crew members, unaware of the full nature of the products being transported and not trained in first response in the event of an incident, can easily become victims.

v) That the evaluation of the environmental damage and the related economic activities (especially fishing and aquaculture), following a chemical spill, is a real challenge.

Group C) Mineral chemicals transported in bulk

Five incidents, involving chemicals obtained from non oil, mineral sources are described hereunder:

1-Case8, 1947, Brest, France, 3158 t of ammonium nitrate.

2-Case9, 1994, Kearny, New Jersey, USA, 490 t of caustic Soda.

3-Case10, 1997, off Brest, France, 114 t of calcium carbide.
4-Case11, 2001, Bay of Biscay, Spain, 8000 t of sulphuric acid.
5-Case12, 2003, La Reunion, 23000 t deoxidized iron balls.

C1) Case8:
When the Case8 cargo of 3158 t of ammonium nitrate started burning after mooring in Brest Harbour and having suffered a series of small explosions, the master of the bulk carrier Case8 wanted it towed away immediately. However, a huge explosion occurred half way to safety, killing 26 people and causing hundreds of casualties, as well as blasting 4000 to 5000 houses and downtown buildings. There was no report of any water pollution.

C2) Case9:
When the barge Case9, loaded with 1200 m³ of caustic soda, was moored at a landing stage in the south of Kearny, New Jersey, USA, with a list of 70°, she spilled 490 t of her cargo in the Hackensack River and Bay of Newark. The pH alongside the barge reached 12 very quickly and came down to 9 three hours later. The pollution only affected the area in the immediate vicinity of the barge. No recovery was possible. The discharge of caustic soda caused a fish kill and the destruction of neighbouring marshes.

C3) Case10:
When the cargo vessel Case10 broke in two and sank silently off the Bay of Biscay at depth of 120 m, its 25 crew sank with it. The vessel was carrying 10 dangerous substances, according to the IMDG Code, plus 1100 t of propulsion fuel (IFO 180). With regard to the chemicals, the main risk was related to the low resistance of the barrels containing calcium carbide at a depth of 120 m (12 bars: acetylene formation in case of water infiltration could possibly induce ignition).
For the phenol, lead oxides, naphthalene, caustic soda, camphor, iodine, resins, solids and paints onboard, the potential risk was likely quite limited in terms of space and time.

C4) Case11:
The chemical tanker Case11 transporting 8000 t of sulphuric acid (D, MARPOL CAT , cat Y), sank in the Bay of Biscay at a depth of 4600 m. When mixed with water, the concentrated acid releases significant quantities of heat. In shallow waters, the water can be brought to boiling. In very deep waters, the pressure would likely prevent this from occurring. Spilled in large quantities, the acid would sink and be diluted in the water. The product is miscible in water in any proportion and would be completely diluted in the long term. No response was possible.

C5) Case12:
In 2003, the Case12 bulk carrier, transporting 21000 t of deoxidized iron balls, noted an increase in the temperature of its cargo. It sailed to La Reunion, as this was the only place in the area where it could seek assistance. It did not have the authorization to berth and remained in Possession Bay to air its holds and to evacuate hydrogen by natural ventilation. This proved insufficient to cool the cargo. Deoxidized iron balls tend to reoxidize, releasing heat and hydrogen in contact with air or humidity. This is why this loading of this type must be carried out with significant caution, i.e. dry loading into clean and watertight nitrogen saturated holds. The principal risk is that of explosion, if hydrogen is produced

and not properly ventilated, and weakening of the ship's structures if exposed to heat. In this case, the authority in charge, moved the ship 10 nautical miles away from Pointe des Galets and, after having evacuated the crew, scuttled the ship, sinking it at a depth of 1700m.

Lessons Learnt :

i) Responders may be faced with families of chemicals presenting very different characteristics and dangers.

ii) The most aggressive acid or soda may cause dramatic damage at high concentrations and generate a toxic cloud. These chemicals, however, are fully soluble in seawater and longer present a hazard from tens of meters to some hundred metres from the spill source.

iii) Some chemicals, like ammonium nitrate, generate far different hazards in air and water. In air, ammonium nitrate is a potent explosive. In water, it is a fertilizer, hypothetically capable of generating, depending of the area and season, either a small, localized phytoplankton bloom, or a major bloom, the consequences of which may be of considerable importance.

iv) Metals, such as deoxidized iron balls, can produce an exothermic chemical reaction in air that would be immediately stopped in water.

Group D) Edible oil transported in bulk

Vegetable oils are classified as Fp (Floating persistent) as their viscosity is > 10 cSt. They are included in the category Y of appendix II of MARPOL. They were not considered as dangerous (MARPOL CAT , cat D, i.e. presenting a discernible risk for marine resources, human health and/or the other uses of the sea) in the marine environment, until January 2007, the date of entry into force of the new IBC code.

Since January 2007, they have been recognized as being in category Y, i.e. "liquid substances which are deemed to present a hazard to either marine resources or human health or cause harm to amenities or other legitimate uses of the sea and therefore justify a limitation on the quality and quantity of the discharge into the marine environment".

Some information of interest was collected on two incidents involving food products, namely:

1-Case13, 1991, Irish Sea, 1500 t of sunflower oil.

2-Case14, 1997, the Channel, France, 900 t of palm kernel oil.

D1) Case13 :

The Case13 incident is an interesting example of a chemical polymerizing in seawater; the sunflower oil molecules polymerized under the action of the waves and, once on the beaches, polymerized oil and sand formed a waterproof aggregate imprisoning wildlife.

Near the wreck, mussels died by suffocation. Also , Mudge et al (1993) showed that certain molecules of the sunflower oil's fatty acids (linoleic, oleic, palmitic) accumulated in the flesh of mussels in a 3 km radius around the wreck.

D2) Case14 :

On 1 October 1997, off the coast of Guernsey in the English Channel, the tanker Case14 was involved in a collision and subsequently spilled 900 t of palm kernel oil. The oil solidified quickly forming an 800 m by 400 m slick. The slick continued to spread and broke up into a series of slicks extending over an area of 20 km long by 4 km wide. Part of the solidified oil came ashore on the Channel Islands and on the Coast of the French Cotentin, where it beached at the high water mark. It was made up of 5 to 50 cm margarine like rubbery balls with a spongy yellow core and a whitish crust.

The slicks were tracked over the 2 days following the spill by French Customs and British Coastguard remote sensing aircraft, using airborne sideways looking airborne radars, housed in pods under the fuselage. Recovery tests were undertaken with surface trawl nets. This spill would have been of paramount importance had it occurred in summer, as one can easily imagine the social impact of wide scale landing of "margarine" balls on beaches at the height of the summer season.

The main difference from a crude oil spill was that palm oil is solid at room temperature. Three factors were investigated: slick drift, and physical and chemical changes to the oil and its dispersion pattern in the marine environment. The locations of the slicks, as indicated by the remote sensing aircraft, were compared to computer generated predictions designed for oil spills. However, computer modelling did not appear to be suited to deal with this kind of oil, due to its solid state.

Oil samples were collected both from the sea and from the beaches, in order to investigate the effect of water on the product. Upon investigation, no change in its physical properties was observed. Small scale testing was conducted to simulate the spill. The oil solidified almost instantaneously into very small particles only a few millimetres in diameter, which later aggregated into "margarine" balls, 5 to 10 cm in diameter. Testing showed that the oil dispersed naturally in the water column which may well explain why a large quantity of the spilled oil seemed to have disappeared. A post spill research programme subsequently elucidated the fact that the physical state of the oil is of crucial importance when a spill occurs. The drift of the slick,

surface behaviour patterns and response equipment and methods are radically different for solid and liquid pollutants.

The example of the Case14 incident is a good illustration of the fate of vegetable oil at sea. There was no significant impact on wildlife. Twenty six tonnes of solid pellets were collected from beaches by hand, a fast and at low cost option. On the whole, some 870 t of oil disappeared, constituting, to some extent, both a source of consumable lipids for the marine flora and fauna and a potential threat as the degradation. Palm kernel oil is likely to produce compounds such as alkanes, esters, aldehydes or alcohols (Hui, 1992), some of which are harmful for marine fauna, like pentane and hexanal (CDCP, 2002).

The very large quantity of oil not recovered remains unexplained. Degradation by bacteria is a possible assumption. Studies carried out in the laboratory on soybean oil and samples of palm kernel oil from the Case14 highlighted this bacteriological degradation. Marine bacteria preferentially break down polyunsaturated fatty acids (C18: 2, linoleic acid, in both cases). The kinetics of degradation of the oleic

acid (C18: 1) is slower. The bacteria first break down palmitic acid (C16:0) with a shorter chain than the stearic acid (C18:0), whose degradation starts later (Le Goff, 2002).
The same results were obtained in sea water by Hui (1992) in experiments on the degradation of vegetable oils in the atmosphere.

<u>Lessons Learnt :</u>
i) Accidental release of edible oil in the open sea generates highly visible drifting slicks.
ii) Slicks drifting in high energy water bodies are quickly dispersed and have no measurable effect on the ecosystem.
iii) However, the same release in a shallow bay may result in the destruction of coastal habitats and hamper beach usage.
As a whole, none of the incidents studied involving edible oil were a source of a major environmental, human health or economic problem.

Group E- Edible solid sinkers in bulk: wheat, rice, etc.
Within the framework of the international marine pollution conventions, food products, such as wheat, corn and rice, are not regarded as marine pollutants. When an incident occurs involving a ship carrying such products, the pollution concern is initially centred on the fuel and oils of the vessel.
Preventing fuel and oil from being released or, if released, from drifting on the sea surface and impacting fishing, fish farming and the coastline is the priority of the first response measures.
A food product is not seen as a pollutant. There is a general belief that it will be good food for marine life. It is only in the second phase that concern extends to the food product spilled, when it remains uneaten and begins rotting.
Some information of interest was collected on two incidents involving solid food products, namely the following:
1- Case15, 1992, stranded with a cargo of rice near the mouth of the Guadalquivir.
2- Case16, 1996, stranded on Lavezzi islands, Corsica, France, with 2700 t of wheat on board.

E1) Case15:
On 27 February 1994, the cargo vessel Case15, coming from Thailand with a full cargo of rice and bound for Sevilla, became stranded on a sandbank in the access channel to the Guadalquivir estuary. The ship could not be moved from its position. It was left spilling its cargo and was dismantled over time by winter storms.
No monitoring of the possibility of organic pollution by rotting rice was undertaken.

E2) Case16:
The Case16 incident shows that a massive discharge of cereals in a marine area will mostly remain in place, smothering the sessile fauna and marine flora of the zone, and will rot on site. The case did not prove to be as simple and inoffensive as first appeared, forcing response authorities to face far more complex challenges than they had originally imagined.
Two months later, decomposition of organic matter appeared, resulting in an exothermic reaction, creating exceptionally favourable conditions for the development of sulphate reducing micro flora. This micro flora contributed to the degradation of the organic matter on the site, with significant production

of hydrogen sulphide (H2S), a toxic gas, which forced the response personnel to don respiratory protection equipment.
The majority opinion is that cereals, such as rice, wheat, corn, are not sources of pollution for the population or the environment. But a massive discharge of cereals in a marine area remain will mostly in place, smothering the sessile fauna and marine flora of the zone, and rot on site, presenting particular challenges to responders.
However, the particular case of the wheat carrier Case16, stranded in a late 1996 storm on one of the Lavezzi islands (Bonifacio Strait, Corsica) is an example where pollution was generated not by the product spilled, but by its transformation through the rotting process.

Lessons Learnt :
i) While an accidental release of edible grain in the open sea and/or in high energy areas has no measurable effect, the same release in a shallow bay may result in the destruction of bottom flora and sessile fauna, buried under a thick coat of organic product.
ii) With time, an organic product in a thick layer on the sea bottom may rot and release H2S, creating the need for an exclusion or protection area around the wreckage.

Group F- Non edible solid ore in bulk: coal
Some information of interest was collected on two incidents involving coal transported in bulk:
1-Case17, 1986, Bay of Gijon, Spain, 100000 t of coal.
2-Case18, 2000, San Pietro Channel, Italy, 14000 t of coal.

F1) Case17:
When the Case17 sank in a storm in 1986, while in the waiting area of Gijón Harbour, the
fore part was towed away to be sunk in high seas, but the fore part remained stranded on a submerged rock half a mile off the San Lorenzo beach, the largest Gijon city beach. During the following months, San Lorenzo beach was regularly soiled by coal dust and pellets mixed with fuel.
Although an impact study conducted by the Spanish Oceanographic Institute concluded that this particular type of coal was not dangerous to humans nor the environment, this repeated nuisance led the authorities in charge to contract the removal of the ship remains, except for the compartmented double bottom, which was left in place to become an artificial reef, after all accessible fuel was pumped out. This solved the coal pollution problem, but not that of fuel pollution.
Sixteen years later, the double bottom began, once again, to release fuel. In the end, it had to be thoroughly cleaned, cut into pieces and removed. In this incident, the pollution due to coal was mostly visual, affecting an amenity beach, with no assessed consequences on local flora and fauna.

F2) Case18:
The coal carrier Case18 sank in the San Pietro Channel (southern Sardinia), in 2000. The
Channel is recognized as an ecologically rich area, with beds of Posidonia oceanica. These were not affected by chemical contamination of the water column, but mainly by mechanical phenomena (smothering of the vegetation, abrasion of the leaves, covering of the sediment) related to the coal.

Chemical analyses of the heavy metal of the content of the coal were carried out. However, the wreck lay in a zone of chronic heavy metal contamination by industrial wastes and it proved impossible to determine the exact origin of the detected chemical compounds.

Lessons Learnt :
i) Spilled coal has no demonstrated toxic or coating effect on waterfowl and marine life, except when in a thick layer.
ii) Coal dust stranded on an amenity beach is unacceptable to the public, but pollution risks/response after a coal spill remain far less important than the risks and response related to the ship's bunkers.

Group G- HNS in bulk from oil distillation

Eight incidents involving HNS obtained through the cracking (distillation) of crude oil and transported in bulk have, to some extent, been documented:
1-Case19, 1984, Adriatic Sea, Yugoslavia, 1300 t of vinyl chloride monomer.
2-Case20, 1988, North Sea, Netherlands, acrylonitrile.
3-Case21, 1991, Adriatic Sea, Italy, 3013 t of 1,2 Dichloroethane and 549t of acrylonitrile.
4-Case22, 1995, access to the port of Zhanjiang, South of China, Styrene monomer.
5-Case23, 2000, North of Batz Island, France, styrene, methyl ethyl ketone, isopropylic alcohol.
6-Case24, 2002, off Sein Island, France, ethyl acetate and cyclohexane.
7-Case25, 2004, Virginia, USA, ethanol.
8-Case26, 2005, Taiwan, benzene.

G1) Case19:
The Case19 was a chemical tanker transporting vinyl chloride monomer, or VCM (GE, MARPOL CAT , cat Y), when she sank in the Adriatic Sea in 1984, in 82 m of water. VCM is an extremely flammable gas, forming an explosive mixture with air. It is a carcinogenic substance (i.e. a substance that can cause cancer). The assumption that the cargo tanks were not damaged made it possible, some three years later (in August 1987), to refloat the ship and to pump out the VCM. A leak of VCM was, however, detected at the beginning of the operations. Were there to have been a massive release of VCM, the refloating would have become very dangerous.
In order to prevent that risk, a hole was bored in the bridge, through which VCM was released on an estimated 3 t/day basis. A concentration of more than 5µg/l was measured in the water column up to 300 m from the wreck. Most of the chemicals solubilised quickly in the sea water. Following several days of release, the divers connected PVC tubes to the previously made holes and released VCM at the water surface, where it either dispersed in the atmosphere or burned. The ship was re-sunk to a depth of 30 m and the 700 t of product still on board was pumped out and transferred to another chemical tanker. The biological monitoring of the benthic communities of the contaminated area started later (1987), including examination of histopathologies and biochemical tests. The results showed no acute toxicity on the organisms taken near the wreck.

G2) Case20:
The Case20, carrying acrylonitrile, sank in the North Sea at a depth of 30 m, 50 miles east of Yjmuiden (near Amsterdam) following a collision with a container ship. When released in the environment,

acrylonitrile evaporates, producing a flammable and explosive cloud. In the event of fire, it produces phosgene, a highly toxic gas. The ship could not be left on site. It was refloated over the next 73 days, with only 25 of those suitable to carry out the work due to poor weather conditions.
The response operation was done properly and correctly. The costs were much greater than expected, but this was mostly due to the bad weather conditions.

The 200 tonnes of acrylonitrile that leaked out did cause damage to marine biota, but with significantly less impact than anticipated. As the concentrations of the pollutant were continuously measured, no unnecessary risks were taken by rescue personnel.

G3) Case21:
The Case21 sank to a depth of 108 m in the Adriatic Sea, 30 km of Molfetta (Italy) with 3013 t of 1.2 dichloroethane (SD, MARPOL CAT cat Y) and 549t of acrylonitrile (MARPOL CAT , cat Y) onboard. The position of the wreck made it non refloatable. Five days after the sinking, acrylonitrile concentration rose to 2.7 ppm, at a depth of 500m directly above the wreck.
A rapid intervention was needed to stop, or at least reduce, the diffusion of the substance.
This operation was carried out by an underwater team of divers and the residual product remaining in the tank was recovered. The acrylonitrile leak was stopped by fitting special joints on the valves of the affected tank and by coating the supports with a special epoxy resin. Once the urgent matter had been dealt with, a cargo recovery project was set up and implemented by expert salvors. Some 900 m^3 of acrylonitrile and sea water were recovered, along with 2750 t of dichloroethane.
At the time, the operation constituted the first of its kind worldwide.

G4) Case22:
On 9 March 1995, Case22, a chemical tanker built in 1994 and loaded with styrene monomer, suffered a collision with the cargo boat Chon Stone N°1, in the access channel to Zhanjiang's Harbour (Southern China). When the ships collided, 230 t of styrene monomer were spilled at sea. The breach was immediately sealed by divers using wooden plugs; however it is likely that some styrene continued to gradually leak out. When immediate human health risks had been eliminated (styrene vapours are neurotoxic), the risks to the sea environment could be characterized by a change in the organoleptic characteristics of the flesh of fish and shellfish. Short styrene monomers are moderately toxic for aquatic life and bio accumulate only to a small extent in the environment.

G5) Case23:
In 2000, the chemical tanker Case23 Sun sank to the depth of 70 m in the north of Casquets, France, while in tow to a port of refuge, with 6000 t of chemicals on board. The crew was evacuated in time. The cargo consisted of styrene (4000 t, FE, MARPOL CAT cat Y), methyl ethyl ketone (MEK, 1000 t, DE, MARPOL CAT cat Z) and the isopropanol (IPA, 1000 t, D, MARPOL CAT cat Z). There were also 160 t of fuel (IFO 180) and 40 t of diesel oil on board. The behaviour of these chemicals in the prevailing conditions around the wreck was unknown.
The studies made it possible to identify the risk of styrene polymerisation, to evaluate the feasibility of a controlled release of the methyl ethyl ketone (MEK) and isopropyl alcohol (IPA), and to study the exposure of marine organisms to styrene.

This illustrated the need for to have a good knowledge of the characteristics and behaviour in sea water of the chemicals transported in order to intervene effectively and safely in the event of an accident.

In this case, it was agreed between the French and British authorities and the ship-owner that the owner would pump the styrene and fuel, and release the MEK and IPA, under the
control of the Authorities. The operations began on 12 April 2001. They allowed the recovery of 3012 m^3 of styrene and heavy fuel remaining in the ship. Work was completed on 31 May, after a 51 day response carried out entirely by ROVs, in challenging sea conditions and in strong currents.

G6) Case24:
In 2002, the Case24, transporting 510 t of soya lecithin (Fp, MARPOL CAT cat Y), 1 652 t of sunflower oil (Fp, MARPOL CAT cat Y), 1 050 t of MEK (DE, MARPOL CAT cat Z) 4 750 t of cyclohexane (E, MARPOL CAT cat Y) 3108 t of toluene (MARPOL CAT cat Y), 500 t of vegetable oil FA201 (Fp, MARPOL CAT cat Y) 2100 t of ethyl acetate (DE, MARPOL CAT cat Z), 4725 t of benzene (E, MARPOL CAT cat Y), 5 250 t of ethanol (D, MARPOL CAT cat Z), en route to Rotterdam, reported a breach on its port side to the Maritime Rescue Coordination Centre (MRCC) of Jobourg, France, following a collision with a trawler in the middle of the night.
The trawler sank quickly and 4 of the 9 crew members died. Two hundred tonnes of ethyl acetate leaked from the tanker before the chemical could be transferred to another tank and the breach could be sealed.
One can only imagine the effect on the coast or in a harbour entry from a wreck involving this cocktail of 9 different food products and chemicals such as that contained on this vessel, two of which are considered to be severe pollutants (benzene, toluene). Luckily, there was no notable pollution identified.

G7) Case25:
The Case25 sank quickly 50 miles off Virginia (USA) to a depth of 80 m, after a fire on the bridge and several severe explosions. It was transporting 11 000 t of ethanol (D, MARPOL CAT Z). Eighteen of the 27 crew members disappeared during the shipwreck and only 3 bodies were recovered. Given that ethanol is completely soluble in water, no containment or recovery was attempted nor was any impact study implemented. The only recognized pollution was that produced by the 720 t of IFO 380 and 166 t of MDO transported by the vessel for its use.

G8) Case26:
On 10 October 2005, the chemical tanker Case26, capsized after colliding with the Nigerian cargo ship off the Northwestern coast of Taiwan, China, sinking in 70 m of water, with a cargo of 3100 t of benzene and bunkers of 85 t of fuel and 16 t of diesel. The 14 crew members were successfully rescued by the Taiwanese Coast Guard.
There was no evidence of a benzene and/or hydrocarbon leak at the surface of the sea.
Water and air samples were collected and analysed daily. Authorities demanded that the ship owner remove the benzene, fuel and hydrocarbons. The shipowner did not comply and, two years later, it was decided that the ship should be detonated.

After looking at various explosives options, to either placed by divers or delivered via torpedos, shot from a short distance, bombing was identified as the preferred method.
On 27 October 2007, an Air Force F16 carrying 4 bombs, made two attempts to explode the shipwreck. Twelve boats and 10 oil recovery vessels were standing by in the surrounding 10 nautical mile area to deal with emergencies. Two more explosion attempts were made by army helicopters. In spite of these efforts, the Samho Brother suffered only damaged to the hull of the bow.
No benzene was detected in the air or water, nor ashore.

Lessons Learnt :

i) A number of spilled oil distillate chemicals are not only recognized as carcinogenic nor as marine pollutants, but can evaporate to form a moderately toxic gas, often capable of producing an flammable and/or explosive mix in air.
ii) Most of these chemicals have no demonstrated toxic or coating effect on waterfowl and marine life, except when in a thick layer.
iii) With some, the risks of fire and explosion onboard, or of a toxic cloud upwind of the ship, along with crude oil in particular conditions, are major risks.
iv) Little is known about the actual marine pollution effect of most of these substances, in practice. The general rule is, to the extent possible, to recover them and to voluntarily release the smallest possible quantity.
v) For ships carrying different products in different tanks, those products in the above category and that are soluble in seawater are customarily released at sea in controlled conditions, with some minor and temporary pollution deemed acceptable, while responders focus on the more dangerous chemicals and products.
vi) Fuel and lubrication oils onboard always receive the same attention as the most dangerous chemical in the cargo. Whenever possible, they must be recovered.