ANNEX

OPERATIONAL GUIDELINES ON SUNKEN AND SUBMERGED OIL ASSESSMENT AND REMOVAL TECHNIQUES

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1 DEFINITION OF SUNKEN AND SUBMERGED OILS

The following definitions are used in this guide:

Sunken oil. Spilled oils that have negative buoyancy and which sink to the seabed.

The negative buoyancy may be due to the high inherent density of the oil, density increase caused by oil 'weathering' or other processes or the adherence of sediment or sand to the spilled oil. The sediment or sand may, in some circumstances, come into contact with the spilled oil while it is at sea, or during stranding of spilled oil on a coastline with subsequent remobilisation back into the sea.

In low current conditions, sunken oil in shallow waters may pool in depressions on the seabed in low current conditions, or be moved along the seabed by prevailing currents. At higher current speeds the spilled oil may be dispersed as relative large, but still non-buoyant, droplets.

Submerged oil. Spilled oils that have neutral or near-neutral buoyancy and which are intermittently submerged below the sea surface for a significant proportion of time in the prevailing sea conditions.

As such, they cannot be reliably detected by visual or remote sensing means from surveillance aircraft or observers in surface vessels. Submerged oils have also been referred to as "overwashed" oils.

Both types of spilled oil behaviour have been recorded at oil spill incidents and a list of such incidents, plus relevant details, is included in this guide.

One important aspect that should be borne in mind is that spilled oil that has sunk or been submerged by prevailing sea conditions at previous oil spill incidents will not have been observed by the normally-used techniques of visual observation or remote sensing for oil on the sea surface. The spilled oil may therefore have been assumed to have naturally dispersed or dissipated and not be recognised as oil sinking or submerging. This is particularly the case for smaller oil spills.

In some instances, it has only been the subsequent oiling of shorelines or birds after surveillance has failed to locate the spilled oil that has led to the suggestion that the oil had submerged and then re-surfaced, or had been transported by sub-surface currents. The conclusion could therefore be reasonably drawn that submergence of some types of spilled oils at sea is a more common occurrence than the records suggest, because the consequences are only observed when significant impacts subsequently occur.

There are several possible processes which can lead to spilled oil sinking or being submerged at sea (Figure 1):

Figure 1: Summary of behaviour of sunken or submerged oils (National Research Council, 1999)

1. Oil sinks

The spilled oil can be inherently more dense than the water it has been spilled into and therefore sinks to the bottom. Oils with density greater than 1.000g/ml (an API gravity less than 10) will be denser than freshwater; oils have to have a density of greater than about 1.025g/ml (an API gravity of less than about 7) to be denser than seawater, depending on the seawater salinity ranging from 36 ‰ and 38 ‰ p.s.u..

2. Oil submerges

The density of the spilled oil is close, or becomes close due to oil 'weathering' (evaporation and dissolution of more volatile components and incorporation of water as a water-in-oil emulsion), to that of the water and it floats very low in the water and can be submerged under the water surface by wave action while in the open sea.

3. Oil floats, then sinks after picking up sediment in the water column

Suspended sediment may adhere to the spilled oil while it drifts and the consequent density increase causes the oil to be removed from the sea surface, sink below the water surface and be deposited on the seabed as oiled sediment. In general, this has only been observed in areas of high sediment loading in the water. However, it appears to be a mechanism for oil sinking in shallow, turbulent waters with high sediment loading.

4. Oil floats, strands, is remobilised and then sinks

Spilled oil that strands on a shoreline may adhere to the shoreline substrate. If this substrate is unconsolidated sediment or sand, the oil may incorporate sufficient sediment or sand so that the density of the mixture is higher than that of the water. Subsequent re-mobilisation of the stranded oil by wave action on a rising tide may then distribute the oil/sediment or oil/sand mixture on the seabed in shallow water. Spilled oil adhering to a rocky substrate may remain below the water as the tide rises.

5. Oil burns and remaining residue sinks

An incident involving a fire onboard a vessel or in situ burning operations may result in the burning of all, or part of, the oil. Light distillate fuels, such as petrol and kerosene, might be totally consumed by the fire. Burning crude oil will often be only partially consumed in any fire, leaving a residue that has a higher density which may sink.

All of these processes have been recorded at various oil spill incidents, see Table 8.

2 CHARACTERISTICS OF SUNKEN AND SUBMERGED OILS

2.1 Viscosity and density

The density of spilled oil is obviously a defining factor as to whether the oil will float, be submerged or sink when spilled at sea. If the density of the spilled oil is close to, but less than, that of the water into which it is spilled, it will initially float, but float very low in the water in calm conditions. In rougher sea conditions, the oil may be submerged with water by wave action.

Low viscosity oils will be naturally dispersed by wave action, but if the viscosity of the oil is high (as well as having a high density) it will be broken up into relatively large 'blobs' or 'rafts' of spilled oil. These will be submerged by wave action and return only slowly to the surface; the majority of the oil may spend most of the time below the water surface.

2.1.1 Oils that have high density

If the density of spilled oil is greater than that of the water into which it has been spilled, it will sink. The density at 15ºC of freshwater is 1.000g/ml and the density at 15ºC of 33 psu (practical salinity units) seawater is 1.025 g/ml. The salinity and density of brackish waters are proportional. Oil will float or sink, depending on the salinity of the water and the density of the oil (Figure 2).

Figure 2. Density and floating / sinking behaviour (Coastal Response Research Center, 2007)

If the current speed is high and the viscosity of the oil is relatively low, the oil may be sheared into relatively small droplets and be dispersed by the currents into the water column and eventually sink over a very wide area. If the current speed is low, the oil may pool in depressions on the seabed.

2.1.1.1 Slurry oils / Carbon black feedstock

Slurry oil is also known as:- Cat Cracked Slurry oil; Catalytically Cracked Clarified Oil (CCCO); Clarified (or catalytic); Decant Oil; Heavy Clarified Oil; Bunker Blendstock; Carbon Black Oil; Carbon Black Feedstock.; RFD Extract; Aromatic Concentrate; Aromatic Tar.

There are only a few oils that have densities greater than full salinity seawater. These are highly cracked oils known as slurry oils or carbon black feedstock. These have been spilled at sea (and in rivers) and have been observed to sink.

Slurry oil is a by-product of catalytic cracking of oil. Catalytic cracking is used in petroleum refineries to break down higher boiling feedstocks into lower boiling components which are fractionated into various distillate streams. The bottom fraction which is known as slurry oil, is passed through a slurry settler to remove catalyst. The resulting brownish-black liquid is known as slurry oil.

Slurry oil typically has a density at 15°C of about 1.075g/ml (0° API Gravity). A toxicity assessment (CONCAWE, 1989) of 15 samples of slurry oil from European oil refineries reported a range of density at 15°C from 1.0687g/ml to 1.1515g/ml. The density depends on the type of crude oil being processed and the operating parameters of the catalytic cracker.

The primary uses of slurry oil are as feedstocks for further processing in coker units at oil refineries or as a component in Heavy Fuel Oils. Slurry oil is used as a component in IFO oil grades. It is used not only because it is a low-value 'by-product' of refining for higher-value distillate fuels, but also because it is extremely aromatic and therefore does not cause precipitation of asphaltenes that are concentrated in the residues also used to blend IFOs. The amount of slurry oil in IFO grades is limited by aspects of the ISO 8217:2005 specification such as aluminium and silicon content (from catalyst that has not been filtered out), density and viscosity.

Slurry oils may also be used in cut-back and emulsified bitumen; feedstocks for petroleum cokes, petroleum pitch and carbon black; dust suppressant road oils; enhanced oil field recovery oil; and rubber extender oils; process oils and ink oils, although use in these applications has declined in recent years.

The majority of recorded incidents have been in river environments. The largest incident however the Gino incident in 1979 when an estimated 30,000 tonnes of Carbon Black Oil spilled from a cargo of 40,000 tonnes from the sunken vessel occurred in a marine setting. Although many of the incidents happened in rivers, the densities of the oils spilled were sufficiently high to cause sinking in full salinity seawater.

2.1.1.2 Heavy Fuel and Crude Oils

A great part of incidents involving sinking or submerging oil implicate the spill of Fuel Oil (Heavy Fuel Oil, Intermediate Fuel Oil or Residual Fuel Oil). Generally, they are the heavy fractions of crude oil obtained after the distillation process. Usually their composition is variable due to the different mixtures realised in the refineries to reach the chemical-physical characteristics requested by international standards.

More than 25 of the incidents listed in Table 8 involved spills of Heavy Fuel Oil, either as bunkers (Bunker C or Fuel Oil No. 6) or as RFO (Residual Fuel Oil) carried as cargo.

Five of these spills occurred in rivers where some of the oil appeared to sink, although this may have been due to the incorporation of sediment, or due to fast currents.

Spilled oil at sea was reported as having been submerged at nine incidents. Oil was reported to have sunk at six incidents after picking up sediment or sand. In some incidents, this was reported to be at sea before stranding, but in the majority of cases the oil sunk after it had been stranded on a shoreline and then was subsequently re-mobilised.

2.1.1.3 Bunker IFOs (Intermediate Fuel Oils)

Bunker IFOs are not well characterised materials, being composed of a variable mixture of distillate and residual materials, but there are some national and international specifications (Lewis, 2003).

Some IFOs, such as ISO RMK 380 and ISO RMK 700, according to ISO 8217: 2005 have a permitted maximum density at 15ºC of 1.0100g/ml, but it should be noted that the permitted maximum density at 15ºC for ISO RME & RMF 180, ISO RMG & RMH 380 and ISO RMH 700 is 0.9910g/ml.

A few IFOs may therefore sink in freshwater because they are more dense, but if they are within the ISO 8217:2005 specification, no IFOs are more dense than seawater and all will therefore initially float if spilled at sea.

Although the ISO 8217:2005 is an international standard, bunker fuel oils that have properties outside of this specification can still be sold.

An example is the "Heavy Oil No. 7" shipped by the Dalian West Pacific Petroleum Industry Co. Ltd, a Chinese company. This is apparently produced to a Chinese standard specification; SH/T0356-1996.

A "No. 7" heavy fuel oil is, logically, 'heavier' than a No. 6 fuel oil, but the ASTM D396-80 Standard Specification for Fuel Oils used in the USA only extends to a No.6 Fuel, although that designation has no specified maximum density as it applies to heavy fuel oils for industrial purposes.

2.1.1.4 Residual Fuel Oil (RFO)

Cargoes of RFO are less well characterised than even bunker IFOs since there are no generally applicable specifications for RFO. The acceptable properties of a cargo of RFO can be a matter of negotiation between the seller and the buyer.

RFO that is traded as a commodity in bulk is Russian M100; a heavy grade of mazut (heavy fuel oil). This should conform to Russian standard GOST 10585-99, although exceptions from the specification may be allowed, subject to buyer approval.

M100 is available in several sub-grades; standard and low ash content; standard and high Pour Point and with a range of maximum sulphur contents. The normal sulphur content is Grade IV (maximum of 2.0% weight S), but a slightly cheaper, high sulphur content (maximum of 3.5% weight S) is also available.

The Prestige was carrying Russian M100 and the relevant properties are given in Table 1 (CEDRE website).

Table 1. Properties of M100 spilled from Prestige

The RFO carried by the Erika was from the TotalFina refinery at Dunkirk. It was a mixture of 10 % of light fluxing oil, 30 % of heavy fluxing oil and 60 % of vacuum distillation residue (CEDRE website). The properties are given in Table 2.

Oil spilled from Erika		
Density at 15°C	gm/ml	1.0025
Pour Point	°C	$+3$
Viscosity at 100°C	cSt	38
Viscosity at 50°C	cSt	555
Viscosity at 10°C	cSt	20,000
Asphaltenes	% wt.	3.78

Table 2. Properties of RFO spilled from Erika

2.1.1.5 Heavy crude oils

Only a small number of the incidents listed in Table 8 involved spills of crude oil. At the Haven incident some of the Iranian Heavy crude oil burned and the burn residue sank. In two cases (Athos 1 and Nissos Amorgos) the crude oil was Venezuelan Bachaquero crude oil. The different densities reported for this oil are not inconsistent; crude oil density can vary and Bachaquero crude oil comes from different wells within the field. The crude oils spilled at the Alvenus incident, Merey and Pilon crude oil, were also from Venezuela. The oil spilled from the Aragon was Maya crude oil from Mexico.

These crude oils would all be described as 'heavy' (having an API gravity of less than 22º) crude oils, but they are far from being the only high-density crude oils.

2.1.1.6 Synthetic Fuels

Synthetic fuels made by coal liquefaction both during Direct Coal Liquefaction (DLC) (hydrogenation – Bergius process started in thirties of the 20th century) and Indirect Liquefaction (Fischer-Tropsch synthesis). During World War II, Germany produced up to 50% synthetic fuels of about 60 millions barrels annually. It is expected that every German wreck from this time can contain synthetic fuel. Fuels produced using direct or modified Bergius or Fischer-Tropsch method were produced later in limited or even large amounts (Sasolburg, South Africa) There are several methods allowing identification or differentiation from natural, of synthetic oils e.g. presence of phenols and lack of magnesium (Mg) which typically accompanies crude oils and oil products.

3 BEHAVIOUR OF SUNKEN AND SUBMERGED OILS

3.1 Evaporative loss

The loss of the most volatile oil components by evaporation to the atmosphere will inevitably cause the density of the oil that remains to increase, relative to that of the original oil. In general, lowdensity ('light') crude oils will lose more components by evaporation than higher density ('heavier') crude oils, because the 'light' crude oils are of low-density they contain a higher proportion of the more volatile (and low density) components than the higher density crude oils.

Evaporation can be simulated by distillation to various temperatures. Distillation to 200ºC is similar to the evaporative loss experienced in a few hours on the sea. A low density crude oil, such as UK Brent Blend (d=0.8359g/ml, 37.9° API), has around 31% by weight of components that will distil below 200ºC, a high density crude oil such as Venezuelan Boscan (d=0.9984g/ml, 10.2° API) has only 4% of components that will distil below 200ºC. Another Venezuelan crude oil, Bachaquero BCF-17 (d=0.9541g/ml, 16.8ºC) will lose 10% weight. The density of the components that distil below 200ºC is approximately 0.7500g/ml.

Spilled Brent Blend crude oil would lose 34.5% volume and the residue would have a density of 0.8812 g/ml (an increase of 0.0453g/ml), while spilled Boscan crude oil would lose only 5.33% volume, but the residue would have a density of 1.0124g/ml (an increase of 0.014g/ml). These densities are shown in Figure 3.

While the incremental change in density due to evaporation of the Boscan and Bachaquero crude oil is less than that of the Brent Blend crude oil, the density of the Boscan crude oil after evaporation is much closer to that of seawater and would be greater than freshwater.

The density of the original Brent Blend crude oil was 81.6% of that of full-salinity seawater and increased to 86.0% after evaporative loss. The density of the original Boscan crude oil was 97.4% of that of the seawater and this increased to 98.8% after evaporation. The behaviour of Bachaquero BCF-17 crude oil was intermediate; 93.1% before evaporation and 96.0% after evaporation.

High density crude oils have an initial density that is close to that of seawater. Even small loses of volatile oil components can cause the density to become very close to that of seawater.

3.2 Water-in-oil emulsification

The incorporation of water droplets into the body of the oil to form water-in-oil emulsions will cause the density of the emulsion to be higher than that of the original oil.

The density of the emulsion will depend on the density of the oil (after the evaporative loss of the more volatile components) and the proportion of water incorporated. The rate of uptake of water is a process that depends on several factors, including asphaltene content (and therefore emulsion stability) of oil, oil viscosity and sea state.

Provided that the oil itself has a density of less than that of seawater, no amount of incorporated seawater can cause the resulting emulsion density to be higher than that of seawater. However, the density of the emulsion can become very close to that of seawater when the density of the oil is high and the proportion of seawater in the emulsion is high.

Figure 4 shows the densities of emulsions as a function of seawater content for oils of densities of 0.8500g/ml to 1.0100g/ml. A typical maximum water content for emulsified oils is 75% volume. Only oils with an original density of 0.9500g/ml produce 75% volume water content emulsions with a density in excess of 1.000g/ml.

3.3 Sediment interaction

Two reviews of sunken and submerged oil behaviour; Michel (2006) and ASMA (2007) looked at broadly the same historical data (mainly from the NOAA, 1992 report), but defined oil behaviour in slightly different ways.

The Michel, 2006 report defines 3 behaviours:

- Heavier than Water/Sank
- Floated, then Sank after Stranding

• Floated, then Sank without Stranding

The pattern of behaviour in the ASMA, 2007 is reported as one, or a combination of:

- Neutrally buoyant emulsion
- Heavier than water emulsion (or oil)
- Mixed with sediments once stranded, then re-suspended and sank
- Adsorption of suspended particulate matter

"Floated, then Sank without Stranding" in the Michel report is similar to "Adsorption of suspended particulate matter" in the ASMA report, and the incidents reported as having these behaviours are presented in Table 8.

3.3.1 Oil / sediment or sand interactions in the water column

Dispersed oil droplets can interact with suspended sediment or sand in the water column leading to the sediment or sand adhering to the oil and the density of the mixture becoming greater than that of the water. The density of the spilled oil may have already been increased by the loss of volatile components through evaporation and by the incorporation of water to form water-in-oil emulsions.

The amount of sediment or sand required to cause the mixture with oil to sink depends on the density of the sediment or sand.

Figure 5 shows the effect of different amounts of wet sand (density = 1.992g/ml) added to emulsified oils of different density with different seawater contents. Lower density oils will require greater amounts of sand to sink and emulsions with higher water contents require less sand to sink than emulsions with lower water contents.

There must be sufficient suspended sediment (or sand) available in the water column, and the conditions must be suitable to bring this into contact with dispersed oil. Negative or near-negativebuoyancy oils near the sea bottom in high energy bottom conditions (strong currents) may take up sand / sediment, thus enhancing likelihood of permanent sunken status.

According to Payne et al., 1987, the variable of SPM (Suspended Particulate Material) concentration appears to contribute significantly to the vertical transport of oil:

- At low (< 10 mg/l) SPM levels, little transport of oiled particles is expected.
- Under moderate SPM (10 to 100 mg/l) levels, significant sorption can occur provided that there is adequate mixing of oil and particulates.
- Massive sinking of oil may be possible under conditions of higher (> 100 mg/l) SPM concentrations (Boehm, 1987).

The dispersed oil may be temporarily dispersed by wave action, i.e. of larger oil droplets that would have re-surfaced, had oil / sediment interaction not occurred.

In a laboratory study, Guyomarch, Merlin, and Bernanose (1999) showed that a mineral load of at least 1.3 to 1.6 grams per litre of seawater is needed to remove oil from the water surface due to oil-mineral aggregation. The threshold concentration is dependent on oil and clay types, their relative concentrations, and water salinity.

Figure 5. The effect of sand addition to emulsified oils of different density containing different amounts of water

Oil/sediment interaction is unlikely to happen in the open sea where the suspended sediment concentration is normally low. However, such interactions may occur at sea when:

- 1. Specific conditions that cause high sediment load in the water column, for example, very rough sea conditions for prolonged periods (such as occurred at the Braer incident (ESGOSS, 1994)).
- 2. Specific locations of high sediment load, for example, river estuaries.
- 3. Shallow water (less than 10 metres deep) with a sediment seabed.
- 4. The surf zone where oil and sand are subject to intense mixing.

3.3.2 Oil-mineral aggregation / Clay-oil flocculation

Oil-mineral aggregation (OMA), also referred to as "clay-oil flocculation", is a process that has been studied in some depth by several different groups. OMA is the gradual removal of oil from a shoreline in the form of oil-mineral aggregates or clay-oil flocs. This process has been proposed as the action that causes eventual self-cleaning of oiled shorelines.

Oil-mineral aggregation formation has been observed in field situations (Owens et al., 1995; Sergy et al., 1999). In general, however, the available evidence seems to indicate that OMA does not play a significant role in the fate of oil in the early stages after oil deposition on the shoreline. Reed, Kana, and Gundlach (1988) concluded that the OMA formation process was not important in the surf zone relative to other transport processes. OMA may, however, play a role in longer-term shoreline processes (Fingas 2001). It may be important in areas where there are significant concentrations of fines, particularly in areas with coarse gravel with open spaces. It may be relevant in longer-term shoreline-oiling modelling.

Crawford et al. (2002) reviewed oil spill fates models including oil-shoreline interaction models and concluded that they still need to better describe the physicochemical processes involved in the remobilization of oil from a beach face during and after the oiling event. In particular, they conclude, the inclusion of the phenomenon of clay-floc formation on beaches would be useful. The

nearly neutrally buoyant clay-oil flocs appear to be mobilized with minimal wave action and could be carried long distances by currents.

To some extent, this process occurring in shallow water has been variously described as OMA, or as clay-oil flocculation by other research groups, and has been the subject of extensive studies. However, OMA or clay-oil flocculation is generally considered to be a longer-term, self-cleaning process of shorelines that contain a high proportion of mineral 'fines'. As such, it is a process that leads to 'sinking' of spilled oil, but only as the wide distribution of oil-contaminated sediments. OMA may eventually happen at many oil spills of almost any oil type (but particularly for low viscosity oils), but is not generally considered to be an oil sinking or submergence process.

3.3.3 Key parameters of oil / sediment interaction

The concentration of suspended sediment in waters depends upon a wide range of physical processes, and on fine sediment being available. There must be sufficient available suspended sediment to interact with the oil. Sediment transport is initiated by wave and current effects on the seabed and by subsequent movement arising from tidal and non-tidal currents, and in shallow water environments there is potential for the prop wash associated with response craft to create the same effect. Suspended sediment concentrations can vary by an order of magnitude over periods of minutes and hours. The concentration also varies vertically (as sediment originates at the seabed) as well as horizontally. Time-series data are thus essential to the effective description and understanding of suspended sediment concentrations for accurate calculations (based on information from the Oceannet website, run by the IACMST (www.oceannet.org)).

The type and size of sediment are also important, both to concentration, and to interactions with oil.

3.3.4 Sand (or sediment) incorporation after stranding on the shore

As illustrated in Figure 5, emulsified, high-density oils require the addition of relatively little sand to become heavier than seawater.

The adherence of sand following spilled oil being deposited on a sandy shoreline, and then the eventual sinking of the oil following subsequent re-mobilisation has been observed at several spills (Table 8) and is probably the most common cause of oil eventually sinking.

This behaviour occurs with heavy crude oils (the Alvenus, Nissos Amorgos and Athos 1 incidents and the burn residue – and possibly crude oil – from the Haven incident) and with HFOs.

The basic requirements for this behaviour to occur are:

- Suitable oil properties; high-viscosity, high density and 'sticky' oils;
- Suitable shoreline substrate; sand (and possible coarse sediment);
- Suitable mixing conditions; either in the surf zone where oil is broken up and mixed with suspended sand, or a tidal cycle that strands the spilled oil, allows it stay on the shoreline substrate surface for long enough to allow it to incorporate sufficient sand for subsequent sinking, and remobilisation. The reports from actual incidents are not always clear as to the time-scale required for this behaviour. Some indicate rapid sinking following energetic oil-sand

mixing in the surf zone, while others seem to indicate a longer time-scale involving the tidal cycle.

The reasons why this behaviour probably does not occur with all spilled oils needs to be considered:

- Lower viscosity oils would most likely penetrate into porous shorelines and not be available for subsequent remobilisation.
- Lower density oils (even when emulsified) would not penetrate into the shoreline substrate to a degree that allowed them to pick up sufficient sand to subsequently sink.

3.3.5 Spilled oil / shoreline interactions

Spilled oil can interact with shoreline substrates such as sand and/or sediment in several ways:

- 1. Spilled drifts impacts the shore, driven by the wind, and is deposited on the shoreline as the tide recedes.
- 2. Depending on the shoreline type, some of the spilled oil may penetrate into the shoreline substrate, while the remainder stays on the shoreline surface.
- 3. The spilled oil that did not penetrate into the shoreline substrate is then re-mobilised on an incoming tide, re-floating at sea to be re-deposited on another section of the shoreline.
- 4. Some of this remobilised oil contains a proportion of shoreline substrate (sand or sediment) that has adhered to it (adsorbed) and the density of the mixture is greater than that of the water and the oil / sand / sediment mixture sinks in the shallows.

As in the previous section, Oil-mineral aggregation is believed to be a process that gradually removes oil from a shoreline in the form of oil / mineral aggregates. This 'self-cleaning' action takes place as very small (micron-sized) oil droplets and very small mineral particles ('fines') form agglomerates, or is flocculated.

5. Some of the sediment may subsequently settle out of the oil.

Spilled oil that strands on shorelines that are composed of sediment or sand may incorporate some of this substrate as it settles on the beach. When remobilised on a rising tide the oil/sand mixture may have a density that is higher than that of the water into which it is transported. The oil/sand mixture will then sink in the shallows.

This behaviour in shallow water may also appear to be due to the mixing of temporarily dispersed oil in the surf zone with suspended sediment.

3.4 Burnt oil residue sinking

There have been a few oil spill incidents when the cargo of a vessel has burned and the burnt residue has sunk. The basic principles of combustion require:

- The flammable hydrocarbons in the vapour phase, or finely divided as an atomised spray;
- The required amount of air to achieve the conversion of the carbon in the hydrocarbon to carbon dioxide (or less optimally, to carbon monoxide) and the hydrogen in the hydrocarbon to water vapour.

• An ignition source.

Burning of crude oil and refined oil products under less controlled conditions, such as those that occur at an incident involving a vessel, may result in incomplete combustion with the formation of a partially burnt residue.

3.4.1 Burning of an oil cargo onboard a damaged vessel

Evaporation of gasoline or kerosene, either from cargoes of these light distillate fuels, or from cargoes of crude oils, will be a source of flammable hydrocarbon in the vapour phase. If air is mixed into this vapour, there is the potential for a fire or explosion if a source of ignition occurs (such as a spark) or is present (fire in another part of the vessel). Stringent precautions are taken to prevent this situation occurring during the transport of crude oil and refined oil products, but they may occur in an accident.

Ignition of the flammable vapour above an oil cargo in tanks will cause the vapour to burn (possibly explosively). The heat generated by the burning vapour may then heat the liquid phase of the oil and cause vaporisation of heavier hydrocarbons that would not normally evaporate at the prevailing ambient temperature. If this occurs, the fire may become self-sustaining; the heat from the fire generates further fuel in vapour form from the oil and the fire continues. The intensity of the fire may be such that it causes significant damage to the structural integrity of the vessel and it eventually sinks.

3.4.2 Burning of spilled oil

If light refined oil products, such as gasoline or kerosene, are spilled onto the sea they will evaporate (very rapidly in the case of gasoline) into the air to generate a substantial cloud of potentially flammable vapour. If no ignition source is present the cloud of flammable vapour will rapidly be diluted with air to below the explosion or flammable limits; there is too much air and not enough fuel vapour to support combustion. The same situation prevails at a spill of crude oil. There may be a risk of fire or explosion in the area where high concentrations of flammable vapour are present. This risk will reduce as the flammable vapour cloud is diluted into the air.

There will be a period of time after the initial phase when spilled crude oil on the sea has the potential to be ignited and subsequently burned. The use of in-situ burning as a response technique has been studied in some depth, particularly in Canada and a very comprehensive review has been compiled (Buist et al., 1994). In-situ burning of spilled oil, even when corralled to the required thickness in a fire-proof boom, will always leave a proportion of residue, composed of the partially burnt heavy components of the spilled oil, after the lighter, more flammable components of the oil have been burnt. These residues can have a high density and some burn residues have a density high enough to cause them to sink. The burn residues can also be very sticky.

Spills of low viscosity crude oils and refined oil products (oils that contain a relatively high proportion of volatile and flammable hydrocarbons) will rapidly spread out to very thin layers on the sea surface if not contained in booms. These layers will either rapidly evaporate (light distillate fuels) or spread to layers that are too thin to support self-sustaining combustion. Higher viscosity oils such as RFO cargoes of HFO bunkers contain insufficient volatile and flammable components to burn when spilled on to the sea.

3.4.3 Key parameters resulting in burnt oil residue sinking

The key parameters that result in the subsequent sinking of some partially burnt residue, due to a density in excess of seawater, are complex and depend on the type of oil, the intensity or ferocity of the fire, the duration of the fire, the location of the oil while burning and other factors. It is not possible to estimate the properties of any residues, such as density, unless the intensity and duration of the fire is also specified.

3.4.4 Pyrolysis

Pyrolysis is the thermo chemical decomposition of organic material at elevated temperatures without the participation of oxygen. It involves an irreversible simultaneous change of chemical composition and physical phase. Pyrolysis may take place when oils burn, particularly at the time of dynamic fire extinguishing or explosions. The uncontrolled and incomplete burning of oils may produce molecules of PAH's (Wolska et al 2011). The kinetics of this process may result in lighter components becoming incorporated (trapped) in the heavier layer, resulting in the mixture sinking. Describing the behaviour of burnt oils is difficult as a number of processes are taking place simultaneously.

4 DETECTION AND MAPPING OF SUNKEN AND SUBMERGED OIL

Figure 6 summarises the different methods, reported in these guidelines, to locate sunken and submerged oil, and Table 3 provides an overview of each methodology.

4.1 Summary of submerged oil monitoring methodologies

Table 3. Options for monitoring submerged oils (National Research Council, 1999)

4.2 Summary of sunken oil monitoring methodologies

Table 4. Options for monitoring sunken oils (National Research Council, 1999)

Although a substantial amount of equipment exists for survey of the marine environment (surface water column and sea bed) including visual, geophysical, acoustic instruments, airborne and satellite remote sensing, water column, in situ detectors, sampling nets, trawls and sediment sampling devices, their use and application to submerged and sunken oil incidents has been problematic, especially when spilled into deepwater, turbid or complex and dynamic marine environments.

Remote sensing techniques such as Radar (SLAR), IR and UV sensors are employed successfully for surface slicks because they either detect the oil on the surface (IR and UV) or measure the wave damping caused by oil on the sea surface. These techniques are not useful for the detection of submerged or sunken oil because UV and IR do not penetrate into water.

4.3 Visual observation

The use of human vision alone is no longer considered remote sensing, it is however the most common technique for oil spill surveillance. In the past, major campaigns using only human visual observations were undertaken with varying degrees of success (Taft et al., 1995). Optical techniques are the most common means of remote sensing. Visual observation can be recorded by the use of cameras, both still and video. In recent years, visible camera observation has been enhanced by the use of Global Positioning Systems information (Lehr, 1994).

Visual techniques have been used to map submerged and sunken oil, such as in the case of the Morris J. Berman (Brown et at., 1998) in clear shallow waters. Biogenic material such as weeds or sunken kelp beds can be mistaken for oil and analysis by experienced personnel is essential. In summary, the usefulness of the visible spectrum for oil submerged and sunken oil in deeper and sediment laden waters (where submergence and sinking may occur) is limited. In shallow and clear water, submerged oil can be detected visually (Figure 7) unless it becomes covered with sediment.

Figure 7. Oil patches in shallow water Lake Wabanum Spill (Photo credit: Merv Fingas, Pat Lambert, Bruce Hollebone, Khrishna, Deana Cymbaluk)

After the oil spill happened in Lebanon in 2006 following the war attack to the power plant of Jieh, in some cases, like in front and southward the port of Byblos (60 km north from Beirut), sunken oil has been observed on rocky and sandy seafloor in very shallow water of no more than 150 cm in depth (Figure 8). Taking into account the occurrence of a tidal excursion of about 50 cm, the phenomenon is probably due to the adhesion to the substrate of weathered fuel oil residues which become heavier because the loss of volatile components and the accumulation of particulate matter and floating debris.

Figure 8. Sunken oil on the seafloor in front the port of Byblos (Lebanon)

At the Morris J. Berman spill in Puerto Rico, the oil patches were readily visible from the air because of the clear water. At the Lake Wabamun spill in Canada, teams used underwater viewing tubes from small boats and kayaks to search for oil on the bottom near shallow wetlands (Figure 9). Standard terminology, photography, and validation sampling are needed for this method to be of value.

Figure 9. Visual Survey at the Lake Wabanum Spill (Photo credit: Merv Fingas, Pat Lambert, Bruce Hollebone, Khrishna, Deana Cymbaluk)

A major problem for visual, video and sonar surveys is the multitude of forms and locations in which oil may settle (Figure 10).

Figure 10. Sunken Oil can be found in a variety of forms (photo credits: ICRAM, ARPAT, Guarda Costiera survey of costs of Lebanon, Coastal Response Research Center)

4.3.1 Divers

In shallow waters a survey of the seabed utilising underwater operators is the best method to define the extent of the concerned area, the status, distribution and amount of the oil residues. It is crucial that the survey is carried out covering the inspected area in a systematic manner describing for each sub-area the main characteristics (status, distribution and amount of the oil residues, etc.). In Lebanon 2006, a survey of the seabed was carried out to define the extent of the area impacted by the sinking of burned oil coming from a power plant in Jieh (Figure 11). Underwater operators and researchers were better suited to this task as the remotely operated vehicle (R.O.V.) was impeded by the almost continuous presence of a thin layer of sediment on the sunken oil residues (Figure 12).

At sites where visibility on the bottom is at least 0.5 m, an underwater video camera has been shown to be a very useful technology (Figure 13). It provides good visual documentation of the distribution of the submerged oil, but only in the field of view (approximately 1m). Visibility is one of the key limiting factors. Most responders do not have much experience in this technology, and they need more information on the different models, configurations, operating conditions, GPS capabilities, postprocessing tools, etc. to make the best choice.

Divers with helmet-mounted video cameras are an alternative. Diver observations are the most common preliminary surveys in most incidents.

Figure 11. Picture reproducing the survey carried out in Lebanon by Italian Coast Guard to map the sunken oil in front the power plant of Jieh (Image realised by Roberto Paganini – Italian Coast Guard)

Figure 12. Sunken oil residues partially covered by sediment

Concerning the use of divers in order to detect and map hydrocarbons on the seafloor, it is interesting to point out the possibility of using a geo-referenced underwater positioning system by which the operator is able to record latitude, longitude and depth of the areas of the sea bottom covered by hydrocarbons. Obviously this technique may be applied only within certain bathymetries.

Figure 13. Remote and diver operated survey equipment (Photo credits: NOAA)

The information obtained, added to the description of the seafloor characteristics (percentage of coverage, thickness of the hydrocarbon layer, etc.) can facilitate the remediation phase.

This was the case of the underwater operations which took place after the grounding of the M/V Kuroshima in Summer Bay, Unalaska island (Alaska), in November 1997. Thirty nine thousand gallons (148 m^3) of Bunker C fuel oil were spilled along the intertidal zone. The strong wave action together with the high tide pushed part of the oil to the bottom of the coastal lake of Summer Bay.

The underwater survey has been performed by means of a Dive Tracker Acoustic Navigation System (DTS) made up of a DTS unit, on the diver's wrist, interfaced with three transponders located in known areas of the sea bottom as their position is provided by a DGPS. Divers provided all the necessary data in order to map in detail the sea bottom investigated and to guarantee a precise and efficient remediation phase (Martin *et al.*, 2003).

See section 6.2 for further information regarding use of divers.

4.4 Electro-acoustic methods

Most of the sensors able to detect oil spilled at sea are successfully employed for the detection of floating oil. The common detectors, in fact, operate at wavelengths that are readily absorbed by water and therefore not able to investigate underneath the sea surface, meaning new technologies are urgently needed to aid the detection of submerged hydrocarbons. In the last years a great interest is increasing in the development of technologies able to detect heavy fuel oil which sink to the sea bottom or stratify in the water column.

4.4.1 Acoustic Sensors and Sonar

These techniques rely on acoustic sounding principles, specifically the differential density and sound speeds of water compared to those of oil or oil/sediment mixtures and the scattering of sound waves from particulate material in the water column (Chivers et al., 1990; National Research Council, 1999).

Side-scan sonar and multibeam sonar systems are frequently considered for mapping the distribution of submerged oil on the seafloor. They provide many benefits, including:

- They can operate in low or no visibility settings
- They provide good visualization of the seafloor contours, which aids in identification of potential accumulation areas
- They provide geo-referenced data that can be used to locate targets and estimate volumes
- They have a good range of aerial coverage
- Systems are generally available at short notice.

However, insufficient information is available to responders to guide them about when this technology may be appropriate and in selection of the best system. Post-processing of the raw data can also be time-consuming.

A systematic assessment of acoustic systems is required to identify the conditions under which they are likely to be effective for detection of submerged oil on the bottom, and how the technology might be improved to increase their overall performance.

4.4.2 Side scan sonar

Side-scan sonar has been used at several spills, but in most cases its effectiveness was inconclusive (e.g., Apex barge spill in the Mississippi River (Weems et al., 1997); the M/T Athos 1 incident (USCG 2005)).

Side-scan sonar was used extensively during the DBL-152 (Michel 2006), yet there are little hard data on the operating conditions of the system, how well it performed initially, and what factors led to the change in performance over time (e.g. whether the oil broke into smaller pieces, whether there was sediment cover on the oil surface). This incident could provide a good case study to evaluate the performance of side-scan sonar, over space and time, if the data were available.

In the Athos 1 incident, sonar was used to detect oil that was pooled on the bottom (because the systems were already being used to search for the submerged objects that holed the vessel). It was hoped it would provide complete coverage of potential oil deposits very quickly. As the data were being collected as part of the investigation of the cause of the spill, the response teams were not allowed to actually view the output. However, survey specialists from NOAA and the Navy Supervisor of Salvage did review the data and reported that it could not be used to identify pooled oil (USCG 2005). It was successful in identifying the dimensions of the trench where the pooled oil was found and recovered.

Like other sonars, the side scan sonar transmits acoustic energy and analyses the return signal (echo or backscatter) that previously hit the sea floor or other objects on the sea floor. The fan shaped acoustic wave is emitted by a pair of side scan transducers. Usually the instrument is positioned on a tow fish but it can also be hull-mounted on a surface vessel (Figure 14) or deployed from a Manned/Autonomous Underwater Vehicle (MUV/AUV), or ROV.

Figure 14. side scan sonar could be mounted on a tow fish or hull-mounted (source: NOAA)

The intensity of the echo is continuously registered and a picture of the sea floor is provided where the objects that lay on it appear dark (strong signal) while their shadow is represented by a light area.

This method has proved to be very effective for identifying geomorphologic structures on the seafloor. The analysis of the return signal intensity gives clear indications regarding the characteristics of the seafloor. The signal is higher for rocks and hard sediments and lower for thin sediments rich in water.

If heavy fuel oil reaches the seafloor a contrast between the clear sediment and the polluted one should be evident. It is possible to imagine two different situations:

1) Presence of fluid oil within the seafloor depressions

2) Presence of tar deriving from accidental or voluntary combustion (burning on site) of oil products.

In the first case the registered signal would be low and comparable to the one coming from muddy substrates. This method would be particularly efficient if applied on rocky or sandy substrates, as it would be possible to evidence the contrast with the oil. This phenomenon has been observed in the field as well.

For the latter situation, the presence of tar is detected especially on muddy and sandy substrata as tar acquires the consistency of hard substrata and can form "cliffs" up to 10-20 cm of height. A digital side scan sonar, with a double operative frequency, which enables, if needed, to run the survey with different resolutions, is particularly suitable for the above mentioned tasks.

Other possible acoustic techniques under development are described in section 8.2

4.5 Fluorosensors

Fluorescence spectroscopy has been shown to be an effective tool for monitoring oil contaminants in water. Because the main constituents of oils are aromatic compounds, illumination of oil samples with ultraviolet or visible light causes the oil samples to emit fluorescence. Fluorescence-based methods have several advantages, including: they are non-contact, sensitive to the presence of aromatic hydrocarbons and easily miniaturized. There are, however, other fluorescing sources that may interfere with measurements.

4.6 Mechanical methods

4.6.1 Sorbent drops

Ad-hoc systems consisting of a weight with sorbent materials attached have been used to bounce or drag for short distances along the bottom in a number of incidents in an attempt to map sunken oil distribution. This method has been used in the US since the 1984 Mobiloil spill in the Columbia River. It is "low tech" but uses materials that are readily available at most incidents (Figure 15).

A more recent development of this has been to deploy sorbent cages in lines in an attempt to identify oil migration and contain oil moving towards sensitive locations such as cooling water intakes.

In later spills (such as the Athos 1) strings of sorbent pads or pompoms have been used with anchors to track across areas to detect where and how much submerged or sunken oil was present. The value of the information gained does not seem to be fully justified by the costs or the time and resources required to deploy, recover and asses the levels of contamination if alternatives are available.

Figure 15. Submerged Oil Recovery System (SORS) and Crab pot oil detectors (Photo credit: NOAA)

4.6.2 Chain drags/V-SORS

These systems are designed to be dragged through potentially contaminated areas in order to detect whether oil is present. Their use appears to be accepted now in the US. Units can vary from a single chain with a few snares, to the large Vessel-Submerged Oil Recovery System (V-SORS) with a 2.5m pipe and 28 chains with many snares (Figures 16 & 17). They have been used at many submerged oil spills to provide information on the location and amounts of oil on the bottom. The systems are dragged along the bottom behind a vessel and somewhat angled through the water column

Their actual value is however difficult to determine. Any oil detected has either passed or, in the case of the larger units dragged along the sea / river bed, has been disturbed such that the equipment does not actually provide data on where oil is but where it was before the unit disturbed the oil distribution.

Figure 16. Chain V-SORS (Photo credit: US Coastguard and Coastal Response Research Center 2007)

A particular version of V-SORS with an hydrodynamic deflector has been used during an oil spill from a refinery in Falconara (Italy) in 2007. This deflector was installed in order to tow the V-SORS with a speed of 2 knts and keep it in contact with the bottom.

Figure 17. V-SORS used in Falconara oil spill by ISPRA

4.6.3 Sediment cores

Different types of sediment cores have been used in the past. Most of the time, the results have been of limited value because the oil distribution was very patchy and the sampling area of the core too small to be effective. Also, they have not worked well when the oil was so mobile that it was pushed away by the impact of the corer on the bottom. They would be most successful when the oil is confined to a specific area and thickly pooled – a rare occurrence.

4.6.4 Sorbent barrier/fence

The concept of a sorbets fence or barrier was originally proposed as a method to prevent suspended oil droplets from entering the water intake. The first design consisted of stacks of crab pots stuffed with snare. The design was revised and fabricated using steel frames and mesh. The sorbent fence can be used in submerged oil recovery operations to detect if oil that was suspended in the water column or moving along the bottom.

5 CONTAINMENT OF SUNKEN AND SUBMERGED OILS

In sea surface spill response the normal procedure is to organise some form of containment once a spill is detected. Containment for conventional spills has a number of purposes. Firstly, it prevents the further spreading and break up of the slick. Secondly, it concentrates the slick making it easier and more efficient to recover with a skimmer. Finally, it fixes the location of (part of) the slick so its location is no longer in doubt. For submerged and sunken oil, containment can serve the same purposes.

Figure 18 Assessment guide of the options for containment of sunken oil (Castle *et al.*, 1995)

5.1 Submerged Oil Containment

Table 5. Sunken oil containment options (Castle et al., 1995)

For containment of submerged oil, booms, surface nets and trawl systems all have been considered and tested. Results have varied but in some circumstances have proven useful.

The most commonly applied equipment has been conventional booms. However, these have usually not been deployed intentionally for submerged oil but simply to contain the expected surface slick. Provided that the depth of submergence does not exceed the boom's draft and conventional limitations for boom containment (current speed etc.), booms can assist in resurfacing submerged oil. This is particularly the case where weather conditions are a feature of the submergence or overwash, where a thin film of water has gathered on the surface of the oil. The only known case where this kind of curtain boom was used deliberately in a submerged oil scenario was to isolate leaking, abandoned barges in a dead-end canal in Louisiana, USA. The use of the curtain boom was successful until local vessel traffic disrupted it.

Silt curtains, pneumatic (bubble) barriers, nets and trawls have all been suggested and some tested in incidents but with varied results. The use of silt curtains requires contractors experienced in the proper deployment and maintenance of these systems (probably a person from within the dredging industry). A silt curtain was used in the Netherlands during an incident involving the release of contaminated water into a port basin. The water will flow through the silt fabric but oil can be contained.

Pneumatic barriers (air bubble curtains) were proposed to protect water intakes, and were applied to a power plant water intake during the Lake Wabamun spill. However, the effectiveness has not been reported.

Nets were applied unsuccessfully at the Bouchard 155 incident but proved effective during the Erika spill, possibly as a result of differences in the characteristics of the oil. Specially designed spill recovery trawl nets have evolved in response to the increased carriage and risks of high viscosity oil spills. Such nets lend themselves to recovery of patches of cohesive submerged oils. The principle difficulty with these systems is detection and rapid response to the submerged oil patch such that the trawl system can recover it before it has moved. Fishing nets have not been very successful for recovery of semi solid tarballs; they are likely to be even less effective with more liquid oils.

During the Puerto Rican spill, involving the barge Morris J. Berman, strings of snare were tied to lines throughout the water column to recover oil re-suspended during dredging operations. However, success was not recorded as there was no method to measure how much oil bypassed the installation.

Several types of filter fences or curtains have been used at spills to either contain oil suspended during recovery of submerged oil from the bottom or to protect water intakes. One such design uses a snare attached to a frame that is suspended downstream of the recovery site (such a design was applied to a coal tar oil spill in the Detroit River where the currents reached 4 knots (Helland et al., 1997). During the M/T Athos 1 spill, a "snare monster" was constructed out of two frames with snares between them. It was originally built to protect water intakes but was only used to monitor for oil suspension during recovery of oil from the river bottom. Geotextile fabric was used to divert oil from the water intakes at a utility power plant at the Lake Wabamun spill, though there is no information on how well it performed. All of these systems were constructed ad hoc, without the benefit of engineering guidelines on water flow rates, filtration rates, etc.

The Western Canada Spill Services (WCSS) conducted trials to evaluate the concepts of sunken oil containment. The trials used a fine mesh net and a sub surface containment net. Both systems were deployed using divers but WCSS concluded that in general it was not confident that these were

effective for containment or assisted recovery. WCSS is continuing to consider the technique and may conduct further work if new concepts or materials are identified and considered worthy of further study (Western Canada Spill Services 2008).

5.2 Sunken Oil Containment

With sunken oil the concept of containment is equally applicable. Where oil is mobile on the sea bed, containment may be able to stop its migration while recovery assets are deployed, concentrate it to simplify recovery and 'fix' the oil so that it can be easily relocated. Even oil movement of a few tens of metres can make redetection very difficult.

The only successful containment of oil on the seabed has occurred naturally, where the oil accumulated in low-flow zones, existing depressions of its own accord.

5.2.1 Trenching/Berming

During the DBL-152, the idea of building a berm/trench or filter fence around the larger patches of oil was considered. However, it was agreed that it would not provide adequate containment as suspended oil would probably pass over the structure.

5.2.2 Seabed booms

There have been some experimental bottom booms built. These work like a regular boom with a heavy ballast to seal on the bottom and a "float chamber" suspended off the bottom. The strategy of containing oil on the bottom, under conditions where it can move or is moving, would be similar to those using booms to divert floating oil to recovery devices. Bottom booming strategies would have deal with a wide range of conditions and oil behaviour, which are usually poorly understood during the emergency phases of a spill response.

6 RECOVERY OF SUNKEN AND SUBMERGED OILS

Figure 19. Assessment guide of the options for recovery of sunken oil (Castle *et al.*, 1995)

Table 6. Sunken oil recovery options (Castle et al., 1995)

The majority of non-floating oil recovery has been conducted without any form of containment being installed. In most cases oil appears to have remained in situ or been able to be tracked as it moved. However, as there is little information on quantities initially identified or later recovered it cannot be verified that recovery without containment is effective. If recovery is to be used without containment then it is clear that rapid recovery is required. A number of technologies exist for recovery of sunken oil but only two companies have looked to develop specialist sunken oil recovery equipment. The first has drawn on its experience as a spill contractor and the second has looked to broaden the application of its dredging systems business line.

6.1 Mechanical methods

6.1.1 Beach Systems

As previously highlighted in this guide, sunken oil can result when oil beaches, picks up sediment and sinks on refloating. Rapid cleaning of beaches can reduce this issue. The techniques of beach cleaning have evolved such that all personnel are aware of the needs to minimise removal of beach material and use of mechanical equipment is limited to assisting and supporting generally manual cleaning operations. However, it may be necessary to consider that oil may refloat and sink. Whilst the use of excavators (Figure 20) will generate large quantities of waste this may be less or equal to that which will be generated in recovery of sunken oil or repeated cleaning of the beach over a extended period of natural resurfacing of the oil.

Figure 20. Mechanical Rapid Cleaning To Avoid Oil Remobilisation

A further technique of beach based cleaning could be applied when oil sinks in very shallow areas. Oil may be released by physical agitation, using air impact from venture lances or by vacuum or pumped recovery (Figure 21), this approach requires appropriate precautions to prevent the unnecessary spread of contamination.

Figure 21. Sunken oil recovery at the Baltic Carrier

6.1.2 Dredgers

The recovery of large quantities of sediment from port harbours and around the coastline is an established business. The use of dredgers has therefore been proposed for a number of incidents involving sunken oil and also employed in other cases of sunken contaminants. Different types of dredgers have been proposed or used to recover oil from the bottom (Figure 22).

Figure 22. Gold panning dredger

Where the oil is solidified, environmental clamshell dredges have been used successfully. Modifications using a large duckbill dredge head have been designed to reduce the amount of water and sediment.

Dredgers are generally designed to remove large quantities of material rapidly and, in most cases, from locations where contamination is not expected to be present. They do not therefore have to be as accurate or careful of disturbance as techniques generally employed in sunken oil recovery. If not carefully controlled, dredgers could result in the removal of large amounts of sediment, which would require storage and treatment due to its combination with the recovered sunken oil. They may also result in the distribution of some material from affected areas to adjacent previously uncontaminated sites. The depth of bed material removed is difficult to keep below 20cm to 25cm without modification, or use of the most modern systems.

The application of this technique should be considered very carefully in light of information collected during surveys of the benthic environment and a subsequent NEBA (Net Environmental Benefit Analysis) assessment which weighs up the likely benefits of the oil removal operations against the potential impacts of the use of a dredger. This assessment would need to take into account the degree of contamination and the likely fate of the oil (e.g. a scattering of sunken tarballs that pose little risk to the environment or a thick and highly persistent semi-solid mat that is completely smothering the seabed). It is worth considering that applying a dredger over wide areas may result in considerable damage to benthic habitats that, depending on the degree of oil smothering, may have recovered naturally. For this reason the use of this type of equipment ought not to be considered in and around sensitive benthic habitats since the damage caused is likely to far outweigh the benefits of oil removal (i.e. due to the removal of masses of sediment, the physical scouring of the seabed and the potential to smother surrounding areas with disturbed sediment, oil-laden or otherwise).

Dredgers are normally limited to a maximum of 50m water depth (dredging beyond this not being required for ports) but some specialist systems do exist for greater depth excavations and mineral recovery. The offshore oil industry has developed systems to meet its needs for excavation of pipeline routes and other operations as well as for removal of drill cuttings and other materials from the sea bed.

A number of dredger systems are available (Figure 23). The most basic is a crane mounted grab, which although simple in design, has poor control of direction and depth of cut.

Figure 23. Clamshell and bucket dredger (Photo credit HELCOM/ Hand et al 1978)

Bucket or hopper dredgers utilise a chain of buckets to dig into, contain and convey the sediment/spoil to the surface where it is usually transferred to barges for transport to a disposal site. This type of dredger removes all material it encounters and can result in considerable disturbance of the surrounding sediment.

Hopper dredges have been proposed in response to sunken oil in the past, but the massive volumes of water and sediment generated, compared to the amount of oil recovered, is a significant factor in the selection process. A hopper dredger was considered during the DBL-152 incident because of the need to quickly recover the submerged oil before it spread (though the oil spread before final plans were developed).

Barge or spud leg barge mounted excavators utilise a single bucket either on a fixed mounting or using a dragline technique to remove material. Again material is transferred to a barge for transport to a disposal site. Depth of excavation is reduced and there is more control over the areas excavated but this is countered by the reduced area that can be swept. This type of dredger is more suited to shallow water operations. A similar system was employed in the Erika incident to clear a heavily oiled area of sediment. An area some 1500 m^2 was cleared in 240 hours (10 days continual working), removing some 800 tonnes of oil and sediment. Excavations were reported to be to a depth of 30cm in the most heavily contaminated area.

Hydraulic or suction dredgers (Figure 24) have replaced other types in many areas due to the speed in removing sediment, reduced mechanical components, improved reliability and reduced maintenance downtime. The system uses a centrifugal pump to convey water and sediment (older systems removed as little as 10 to 25 % sediment but modern designs have increased this to 80% reducing the recovered water issues) up a trailing suction pipe to the vessel. Pipes vary from 15cm to 1200cm in diameter and lengths are sufficient to allow depth of up to 50m, or even up to 100m deep with some modern designs. Some are fitted with cutter heads for operation on more resistant sediments.

Figure 24. Mechanical hydraulic dredger (Photo credit Helcom)

Material can be stored on the dredger vessel or transferred to other craft. Storage on the vessel, together with sophisticated dynamic positioning and thrusters systems, allows for self contained and efficient operation even in busy shipping lanes. Suction dredgers were used during the Erika to sweep areas with lower concentrations of oil.

Pneumatic dredgers (Figure 25), such as the Pneuma system, use hydrostatic pressure and compressed air submersible pumps to recover sediment (with low water contents 20% typically). There is no theoretical depth limit for these systems and they have been used in removal of drilling cutting and other contaminants around offshore oil structures. Such a system was used in the Haven incident. In this instance a remotely operated vehicle (ROV) cutter assembly had to be developed to cut the oil into manageable chunks.

Figure 25. Pneumatic dredger which generates less turbulence (photo credit: Helcom)

During the T/B Morris J. Berman spill, two small dredgers using centrifugal vane pumps and rotating dredge cutter heads were employed to recover submerged oil in two small embayments, with good success (Burns et al., 1995). Large, onshore pools provided the capacity needed for decanting. In the Irvine Whale a detailed assessment of the dredging options was made and is shown below.

Figure 26. Analysis of dredger recovery options for the Irving Whale

Dredging is the fastest method for removing sunken oil from the bottom, but is likely to generate very large volumes of oily water and sediment that must then be handled, treated, and disposed of. Even under careful control, dredgers often remove the top 0.5m of material, removing and contaminating a large amount of clean sediment. Logistics and costs are reduced if the material can be handled on land, compared with using barges or temporary storage and separation. Time can be of concern because oil that is still fluid could be re-mobilized by storm waves, increased river flow following heavy rains, or ship traffic.

6.1.3 ROV and Mini Submarines

Long-term diving operations are inherently dangerous, and they become more so at increasing depths. Remotely operated vehicle (ROV) technology has expanded into many applications. ROVs were modified to hot-tap the hull of the wreck of the T/V Prestige and pump the oil off at 3,500 m depth, albeit at great cost. The Remotely Operated Lightering System (ROLS), which operates as a diverless hot-tap and pumping system to remotely recover liquid products from the tanks of sunken vessels is a proven technology that could be built upon. These systems have allowed sustained operations and observation of the sea bed and as a result offer a potential capability for sunken oil detection and recovery. Please see also details of recovery devices under development, section 8.3.

6.2 Manual methods

6.2.1 Divers

Divers have been utilised in a number of incidents both directly to recover more solid oils and in combination with recovery devices for more fluid oils.

Divers have a number of obvious advantages over other equipment in terms of detecting and recovering oil. The amount of sediment and water collected with the oil is low, so post-recovery treatment is reduced. Divers are able to detect and collect small scattered pieces of oil. They can place oil directly into storage containers. In addition to these approaches being more 'selective' in the recovery of oil without excessive amounts of sediment, they are also likely to be far less damaging to benthic habitats and the organisms found there when compared with dredging. Hence divers and diver-operated devices would be more appropriate for sensitive habitats.

However, the duration of dives is limited, particularly in deeper water and at greater work rates. Divers are only able to survey and recover oil from a relatively small area and recovery rates are slow. The potential for the oil to spread to other areas may force a more rapid recovery strategy. At greater depths and in high suspended sediment areas, visual identification of oil is difficult. There is variation in capability between different divers which effects oil identification and recovery rates. Regular decontamination of divers and their equipment can be time-consuming and reduce the efficiency of operations.

Divers have been used in a number of incidents including Bouchard 155, Morris J Berman, Fenes (a cargo of 2200 tonnes of wheat which threatened to smother local seabed biota), Vologoneft, Erika and in the spill during the Lebanon war of 2006. In these incidents divers were employed to use manual techniques. Oil or, in the case of the Fenes wheat grain, was recovered to containers on the sea bed. This technique minimises recovery of sediment as divers have a high degree of dexterity in the operation of hands or tools and are disinclined to create excess work for themselves. The
technique also minimises the quantities of water recovered reducing the need for surface separation of waste streams and processing of water.

During the Volgoneft 248 divers were engaged to recover sunken oil in shallow waters. An important element of reported success was the contract. This incentivised divers, who were paid according to the oil content of the material recovered and on a sliding scale as remaining oil become more scattered. Although often quoted as a success, it should be noted that of 850 tonnes potentially available for recovery only 368 tonnes (43%) were recovered.

In Lebanon (2006) clean up operations were conducted following the grid prepared within the survey (Figure 27), a number of 30 m^2 squares marked on the surface by buoys.

Figure 27 Grid prepared for Lebanon clean up operations

Figure 28 Manual recovery of sunken oil in front Jieh (photo credit: ISPRA)

The underwater operators working manually collecting the bituminous residues in "big bags" of one cubic metre of volume placed on the seafloor utilising 50 litres jute bags; as the big bag was filled up, it was recovered by means of lifting inflatables (Figure 28). The estimated total quantity of oil residues lying on the seafloor of the stretch of sea facing the power plant was about 500 m^3 , the total quantity of product collected from the seafloor was about 350 m^3 . See section 6.2.3.3

The manual recovery of sunken oil appeared to be the only system useful to collect solid and semisolid product (Figure 29).

During the days following the Haven accident (1991) actions were taken in order to deal with the sunken bitumen. Investigations of the sea bottom near the wreck (75 m depth) were carried out by means of side scan sonar, sub bottom profiler and remotely operated vehicle. The results indicated that the sea-bottom within 1,000-1,200 meters from the wreck was affected by tar depositions 10 cm thick, covering an area of 120,000 m2. Oil residues that were dispersed at less than 20 meters depths were re-suspended and washed ashore during storms, affecting the beaches and thwarting the clean up operations. In order identify the extent of this problem, surveys were carried out with the aim of locating the oil residues sunk within a depth of 20 meters. Several techniques were expressly developed and tested in order to avoid alteration of the morphology of the sea floor and further damage to the underwater flora and fauna. Manual recovery by divers was the most used method and the one that proved most flexible and successful, since it could be applied to all kinds of sea floor. Manual removal was supplemented by gathering oil residues by means of a specially adapted sort of

steel clam hook. 200 m3 of oil residues were collected from the sea bottom during 1,500 man/days of work (Morucci et al., 2002).

Solid product **Product releasing from the sediment** Figure 29 Images of the different typology of oil encountered on the seafloor in front the powerplant of Jieh (Lebanon)

6.2.2 Diver Directed Recovery Device

Another common use of divers is to direct a recovery device. This increases the area being treated whilst reducing diver workload. Divers are most commonly used to direct vacuum, air lift or negative pressure pumping (a positive displacement pump can be used to create a negative pressure and draw material in, alternatively submersible pumps of the centrifugal or positive displacement design will achieve this effect.). In some cases a combination of these may be used in a single system, particularly when operating at greater depths.

Systems utilising these technologies have been employed on a number of incidents. In the Morris J Berman initial operations used vacuum systems which were replaced by 3 generations of pumped systems as efforts continued to refine and improve efficiency. However, this incident also shows a typical trend: the initial systems proved insufficient to recover the material, but the replacements were uncontrollable by the divers and required the removal of the diver for safety reasons (thus losing the control over the material being recovered).

Figure 30. Filtering system to separate sediment/oil from the water utilised

Removal by pump and vacuum systems have historically been the most successful removal strategy for sunken oil. Such systems can include vacuum trucks, units mounted on barges, and submersible pumps. They often are diver-directed and the suction head is modified so that the diver manually opens and closes the valve. The oil must be liquid, or made liquid through the application of heat or mechanical agitation with the sediment and water, to be pumped. As large volumes of oily water are generated, there must be facilities for oil/water separation and discharge of the separated water back into the water (Figure 30). Separation can be very problematic for some oils, especially when they are heavier than water and only part of the oil tends to re-float. During the Morris J. Berman spill, vacuum removal was effective but very slow.

Diver-directed recovery devices ideally allow control by the diver, either through good communications with the surface or by being sized to allow them to be controlled easily (with the disadvantage that this may reduce recovery rates) see figure 31.

Figure 31. Diver operated suction head or stinger with diver controls (Photo credit HELCOM and Tornado Motion)

Sunken oil may become buoyant again if it can be separated from the sediment and given impetus to move, diver-directed equipment could be utilised for refloating sunken oil. For many years, the maritime archaeological and salvage industries have utilised a technique called airlift, or venture. A stream of air is released at the base of a pipe. The air rises and moves towards the surface. This creates suction pressures which creates an effective vacuum to lift sediments and oil. This can cause sediment and oil to be released in to the water column and the oil may resurface. Resurfaced oil is contained and recovered by conventional means. However, the window of opportunity for recovery may be limited as incorporation of air could be a factor in the oil's renewed buoyancy. A variant of this technique (using an impact lance to provide the lifting air under patches of oil) was used at the Erika incident (Figure 32).

Figure 32. Impact lance used in the *Erika* incident (photo credit: CEDRE)

It is possible to recover material through a hose close to the airlift using this technique. However, such a system typically recovers large volumes of water (in some cases up to 100 times the volume of sediment recovered). To be efficient, water depth of more than 10 meters are required.

In utilising an air operated sucking device on the seafloor, great care has to be given to the need of minimizing the accidental collection of sand, a crucial issue when considering the volumes and quality of wastes to be treated as well as with respect to the environmental damage the clean-up operations might add.

6.2.3 Diver Health and Safety

Divers may become exposed to the oil by inhalation, ingestion or absorption. The oil composition and the weathering process it undergoes (solubility, degradation, evaporation, etc.) will determine the level of hazard (Amson 1991).

The main objectives of safety measures are to minimise the risk of inhalation, and skin contact with the oil. Hydrocarbon molecules can penetrate both suit materials and the diver's skin, mucous membranes are the most vulnerable body regions. Therefore these must be isolated from the source of contamination. Equipping operators with suitable diving support systems (including both respiratory and physical protection) must be the primary concern.

6.2.3.1 Breathing Apparatus

Diving with standard SCUBA equipment (a half-face mask and a mouthpiece regulator) provides very little protection for a diver. The diver's mouth is in constant contact with water, exposing diver to contaminants which can enter either via the mouthpiece or via water refluxed through the exhaust valve.

A full-face mask offers a reasonable level of protection to the mucous membranes of the eyes, nose, and mouth. It can be configured to operate with compressed gas SCUBA tanks, affording the diver freedom of movement. Most full-face masks can also be configured to operate from surface-supplied compressed gas, which increases endurance but restricts mobility compared to SCUBA. A full face mask which incorporates a positive-pressure regulator will help eliminate water entering the mouth. However, a full-face mask offers no protection to the Diver's head, neck, or ears.

Rigid Helmets (Figure 33) protect the diver from contaminated water, as they may be coupled to a dry suit. In this case the level of protection for divers is improved. However, the main drawbacks of using rigid helmets are the high rate of air consumption, which requires a supply boat with air compressor on board, and the reduced mobility of operators. In water heavily contaminated by petroleum products, some latex components of the helmet are highly susceptible to degradation, requiring frequent replacement (Sea System Command, US Navy, 2008).

Figure 33. The Kirby Morgan helmet

6.2.3.2 Suit and gloves

In highly contaminated water wet suits offer little to no protection as the skin is directly exposed. Foam neoprene suits should not be used as they can absorb large amounts of contaminated water making decontamination hard.

Dry suits offer substantial protection in highly contaminated waters, although a dry suit is subjected to degradation as well. A suit that has been degraded by contaminants may exhibit swelling of the material, colour and thickness changes, stiffness when dry, and exposure of the underlying fabric. Suits demonstrating any of these changes should not be reused.

Chemically resistant waterproof gloves should be used during diving in contaminated water. Gloves should be positioned over cuff rings on the sleeves of the dry suit. If the Diver is likely to encounter bulky, adherent contaminants during a dive, a disposable over-suit (e.g., TYVEX[®]) may be used. Such disposable hazardous protective suits can be secured on a diver after he has been outfitted with the entire diving rig. No effort to make the oversuit watertight should be attempted; such an attempt could cause buoyancy difficulties i.e. by creating air pockets (U.S. Environmental Protection Agency, 2010).

6.2.3.3 Other safety measures

Obviously, all other diver safety measures that are valid for generic underwater activities have to be followed. For the recovery of sunken oil, it is advisable that residues are collected in one cubic meter bags, placed on the seafloor utilising 50 litre jute bags (see Figure 28). As the larger bag is filled up, it should be recovered by means of lifting inflatables. In this way the underwater operators remain at a fixed depth avoiding the need to go up and down continuously (the so called "yo-yo" effect).

The clean-up of personnel and equipment, either onboard the supply vessel or on the nearest shoreline, will need careful planning.

The monitoring of all underwater activities, through an ROV or MUV, may assist in assessing safety of operations.

6.3 Assessment of technologies actually employed

Table 7 is a summary assessment of some of the techniques used at the DBL-152 and M/T Athos 1 oil spills.

Table 7 Assessment of detection and recovery techniques of submerged oil (Michel 2006)

7 SUMMARY OF INCIDENTS INVOLVING SUNKEN OR SUBMERGED OIL

Table 8 Summary of incidents involving sunken or submerged oils (MCA 2009)

7.1 Summary of responses to submerged and sunken oil incidents

Torrey Canyon

The Torrey Canyon spill in March of 1967 was one of the first to have issues of sunken oil.

Oil impacting on the coastline which had not been observed moving on the sea surface, or arrived some time after bulk cleanup had been completed, was attributed to submerged and sunken oil. This was supported by diver surveys which identified isolated areas of sunken oil. However, during the incident attempts were also made to deliberately sink oil as a response strategy (Wardly Smith 1967, Admiralty Oil Laboratory, 1968, Griffith Dde G, 1969, Simpson A C, 1968, McKay A C, 1967, Beynon L R, 1967).

SS Sansinena

In December 1976, the Tanker SS Sansinena exploded in Los Angeles while loading bunker fuel oil with an API gravity between 7.9° to 8.8°. This resulted in a large pool of sunken oil at the incident site, which was confirmed by diver surveys to have collected in depressions up to three meters deep.

With a large quantity of oil in a known location recovery operations were initiated utilising vacuum trucks and separation tanks installed on a barge. It was planned that divers would manoeuvre the suction heads but this proved difficult, particularly as the divers could not control the suction rate directly. The suction heads were replaced by those utilizing hydraulic pumps which allowed greater control. Using the new heads, the divers encountered oil and sediment issues which resulted in them directing the pumps by "feel". Following this, special pumping units were designed, which incorporated a different type of hydraulic pump, and were intended to be used without diver guidance. The new technique was found to have limited applicability except for large pockets of pooled oil. In total, nearly 675,000 gallons of the sunken oil had been recovered to this point. Finally a suction head and pump device was designed on-site to address recovery of the remaining oil. By the time it was ready it was necessary to use divers to direct the unit as some of the oil pools had become silted over, making the oil difficult to locate.

This evolution of recovery techniques during an incident is typical and makes the determination of the ideal recovery system difficult. (Hutchison J.H. & Simonsen B.L., 1979, . NOAA, 1992. Oil spill Case Histories, White W.W. & Kopeck J.T., 1979).

Mobiloil

Later in March 1984, the tanker Mobiloil spilled 168,000 gallons of a Heavy Fuel Oil No. 6 (API gravity of 5.5°) into the Columbia River. Due to the density of the river water (freshwater), the majority of the oil sank and moved along the riverbed, being transported by the river currents, often within one meter of the river bottom. The mid-water oil rose to the surface once the salinity of the water increased near the river mouth. This was the first US spill where oil tracking techniques were focused on submerged and sunken oil. Tracking and location of the moving missing oil was rudimentary with weighted sorbents being used to attempt to fix oil on the river bed (Kennedy, D.M. and Baca B.J.. 1984).

Barge MCN-5

In January 1988, the tank Barge MCN-5 capsized and eventually sank in 40 m (120 feet) of water in Puget Sound near the Rosario Straits. The MCN-5 carried heavy cycle gas oil with a specific gravity of 1.086. During the incident the heavy cycle oil was released and sank. Due to heavy currents and tidal changes in the area, initial response efforts focused on the sunken barge and its remaining cargo. Experiments were conducted to observe the oil behaviour in the water column and predict its movement. As in the Mobiloil spill, weighted sorbent pads were used in an effort to map the extent of oil on the bed (Yaroch, G.N. and Reiter, G.A. 1989).

ESSO Puerto Rico

In September, 1988, the ESSO Puerto Rico released 23,000 barrels of carbon black feedstock (API gravity of 2.0° to –1.5°) while travelling along the Mississippi River toward the Gulf of Mexico. The carbon black feedstock rapidly emptied out of the cargo tank and into the river. The oil appeared to be churned into tiny globules and droplets by the action of the vessel's propwash. The oil quickly dissipated with the river currents. Again weighted sorbent pads were used in an attempt to map and fix oil locations. Except for a 10 barrel pool of oil directly below the vessels final anchorage point, only small traces of material were found and these were limited to deep locations along the riverbed (Burns, G.H.,et al . 1995).

Presidente Riviera

In June 1989, the M/V Presidente Riviera ran aground on the Delaware River spilling No. 6 fuel oil (API gravity between 7° to 14°). The oil congealed into pancake-like, tar globs that floated with the river currents. The thick, sticky nature of the product made it very hard to physically remove from both the water and the shorelines. Vacuum trucks and conventional skimmers were ineffective because of the oil's viscosity. Supersucker trucks were only able to pick up small chunks of oil, but were slow process and cleanup/ maintenance of the equipment was difficult. One of the most effective methods of oil recovery in this incident was found to be the use of a fishing vessel with a stern trawl net. This was successful in recovering 8 tons of oil and oiled debris along the river (NOAA, 1992. Oil spill Case Histories, Wiltshire G.A. & Corcoran L., 1991).

Tampa Bay incident

In August 1993, three vessels collided at the entrance to Tampa Bay, releasing an estimated 325,000 gallons of No. 6 fuel oil, with an API gravity of 10° to 11°. The oil weathered on the water surface for nearly 5 days before it came ashore during a storm. Surface oil and shoreline oiling were successfully removed; however, thick mats of sunken oil were found in nearshore subtidal habitats. In several areas, the sunken oil was removed using vacuum transfer units mounted on barges. Diver and aerial surveys found numerous areas of mobile tarballs, pancakes and three mats of sunken oil ranging in size from 150-200 feet long, 10-20 feet wide, and up to two inches thick. The mats may have picked up sediments in the water column or after being stranded onshore. The sunken oil remained on the bottom and had the consistency similar to peanut butter. Attempts to remove the sunken oil included various vacuum-pumping strategies, which failed due to the viscous nature of the oil. After further careful study and evaluation, it was determined that manual removal by divers was the most feasible option for certain areas. However, the offshore mats were not removed, and oil continued to wash ashore for at least six months following the spill and was removed by conventional beach cleaning.

Morris J Berman

In January 1994, the Morris J Berman barge grounded off Puerto Rico releasing a group V fuel oil (API gravity of 9.5°). Although much of the oil floated, extensive quantities submerged and sank and were found in both offshore areas and in sheltered bays

Identification was aided by the affected areas having clear and shallow waters. The submerged oil did not emulsify and remained fluid enough to flow with a consistency described as similar to maple syrup. Over time the oil became more viscous and mixed with sediments in some areas. Some oil was observed to refloat every afternoon as a result of increased wind generated currents and the heating of the oil and water by the sun. This mobile sunken oil complicated the cleanup response. Three different methods were used to recover the submerged oil: diver-directed vacuuming of the more liquid oil; manual pickup by divers for the more viscous patches; and dredging. The diver-directed strategy was effective but slow due to the need to respond to moving targets. Dredging was finally used to recover the remaining submerged oil. This resulted in increased amounts of sediment being recovered but eliminated the ongoing problem (Burns G.H. et al 1995, Lehman S., 2006. NOAA, 1995. Petrae, Lcdr. Gary, 1995, Ploen M., 1995, Vincente, V. 1994).

Jieh Power Plant, Lebanon

In July 2006, during the conflict in the Eastern Mediterranean, a major oil spill occurred at the tank farm of the Jieh Power Plant, located some 30 km south of Beirut, in Lebanon. During air raids a number of storage tanks containing Intermediate Fuel Oil were damaged and caught fire. The fuel oil that was not consumed by fire on land entered the sea, an estimated 15,000 tonnes, causing an oil spill which continued moving towards the north, following the general pattern of currents in the eastern basin of the Mediterranean Sea. A proportion of the oil sank as a consequence of the fire. Divers were deployed to collect the oil manually – see section 6.5 for further details.

MT Velopoula

In July 2004, as a result of a flexible hose rupture at an underwater manifold, the MT Velopoula lost an estimated 60 tonnes of Heavy Fuel Oil in Port Dickson, Malaysia. Diver operations were complemented by the use of a crane operated 8" internal diameter high capacity air lift system with annular air injection, a large diameter (6") delivery hose, and a 'hood' to increase the width of the sweeping swathe. Strong subsea currents moved or buried significant quantities of oil, prior to the receipt of the interpretation results of a sonar side scan survey carried out to determine probable locations of oil.

The above descriptions are from the best documented cases. They clearly show that the scenarios are very different and that solutions from one incident are not necessarily applicable to the next. They also demonstrate an issue with the identification of sites where oil has accumulated and its continuing mobility. In addition, oil may show both floating and non-floating behaviours during an incident: some parts may submerge whilst others sink and in some oil cases oil may have initially submerged, later sunk, refloated, re-submerged and sank over a number of cycles.

A full list of the incidents identified in this guide, plus relevant details, is included as Table 8 of this report and in the reference section.

8 RESEARCH AND DEVELOPMENT

8.1.1 Laboratory studies of oil / sediment interaction

Spilled oil / sediment interaction behaviour has been the subject of extensive programmes of work, mainly for the US MMS (Minerals Management Service) concerned about potential oil spills in Alaska and the Gulf of Mexico

Payne et al., 1987 and Payne et al. 1989 carried out oil droplet-SPM (Suspended Particulate Matter) interaction experiments with an apparatus illustrated in Figure 34.

The reaction vessel was normally a 4-L glass beaker, although a 10-L beaker was used on occasion. Volumes for reaction solutions were either 3.5 or 9.5 L in the 4- or 10-L vessels, respectively. The shaft and propeller connected to the variable-speed motor were used to generate specified turbulence levels in the experimental reaction solution. Torque and revolutions-perminute (rpm) generated by the propeller were recorded with a torque meter and an rpm-counting device connected in-line between the motor and the propeller shaft. The torque and rpm measurements were used to estimate values for energy dissipation per unit time in the reaction solution.

These SPM types included eight natural sediments, one natural marine SPM and two commercially available particle phases. Immediately prior to experiments, all of the natural sediments were presized with a 53 μm geological sieve and only particles passing through the sieve (i.e., particles < 53 μm in diameter) were used. Dispersed oil droplets in aqueous phases for experiments were prepared with a defined protocol. The protocol involved mechanical blending of a specified amount of oil in 750 ml of 0.4 pm filtered water in a commercial multiple-speed blender.

For experiments containing both dispersed oil droplets and SPM, a volume of a parent SPM solution was added to the stirred reaction vessel containing an appropriate volume of 0.4 im filtered water. The volume of parent SPM solution added to the reaction vessel was adjusted to ensure that number densities of SPM particles would be substantially in excess of those for dispersed oil drops.

During a stirred vessel experiment, each 50 μL aliquot collected over time was transferred onto the middle of a microscope slide. The microscope slide contained two stacked cover slips at each end. The height of the stacked cover slips was approximately 0.5 mm. A final cover slip was then placed on top of the end stacks, effectively "capping" the sample and providing flat upper and lower surfaces to the water / oil / SPM droplet. At the Stokes rise velocity specified above for 5-pm diameter oil droplets (i.e., 15 mm/hr), all "free" oil droplets in the sample on the slide would reach the upper cover slip in approximately 100 sec. In contrast, oil/SPM agglomerates and "free" SPM on the slide would sink to the bottom of the "capped" sample.

Figure 34. Apparatus used by Payne et al., 1987

8.1.2 Studies of oil / shorelines interaction

There have been numerous studies on the interactions between spilled oil and shorelines and Etkin et al., 2007 provides a convenient, comprehensive and up-to-date summary of these studies with Appendices on the following topics:

- Shoreline oiling classifications and shoreline types
- Shoreline sediment grain size distribution
- Studies on oil loading, penetration, retention, and holding capacity
- Shoreline oiling in snow and ice
- Shoreline oiling on peat shorelines
- Shoreline oiling with heavy oils
- SOCSEX studies (Subsurface Oil in Coarse Sediments EXperiments).
- Oil weathering processes after stranding
- Oil removal by wave action
- Oil re-floatation
- Persistence
- Subtidal persistence
- Impact of marsh vegetation
- Oil-mineral aggregation
- Shoreline oiling modelling
- Shoreline oiling by shoreline length
- Shoreline cleanup assessment team (scat) processes
- Test tank testing

Many studies have been conducted on the oil loading, penetration and retention of different shoreline types and the examples given here were from the appropriate Appendix in the Etkin et al., 2007 report and a review of the original publication.

Most of these studies have aimed to determine how much oil is retained by a beach, not how much of the beach material can adhere to the spilled oil to form a mixture that can subsequently be remobilised by the next tide. A combination of oil properties, such as adhesion and viscosity, and sediment properties, particularly grain size and sorting, affect oil penetration and retention in beach sediments. Long-term retention of subsurface oil in sediments is largely determined by initial oiling, but any oil that can penetrate fine-grained or mixed, sandy-gravel beaches is likely to be retained in the subsurface of those beaches.

Gundlach et al. (1978) showed that depths of oil penetration in the Urquiola spill site in Spain increased significantly with increasing sediment grain size. Pertile (1986) described stranded oil on remote shorelines:

- The penetration of an oil slick will vary as the granular size of the beach sediment. Finergrained sediments allow less penetration than coarser-grained sediments, such as gravel.
- Oil penetration increases as oil viscosity decreases.
- Oil thickness on sediment increases with grain size and the age of the spilled oil.

High-viscosity, high-density emulsified oils will therefore not penetrate into fine sediment beaches and only slightly into sandy beaches. No mention is made of spilled oil retaining some beach material when it is remobilised.

Humphrey, Owens, and Sergy (1993) concluded that the transition from maximum oil capacity (or first loading) to residual loading, without storm interaction, is the critical period. Oil is removed during a tide cycle by washing of particles. The rate of removal depends on the oil viscosity and the attractive forces between the oil and the substrate.

Owens and Sergy (1996) published a state-of-knowledge review of oil on shorelines, including oil behaviour, fate, and persistence. The following conclusions were made on oil penetration:

- Oil more easily penetrates coarse-sediment (pebble-cobble) as compared with fine-sediment (sand/granule) beaches.
- Penetration is increased in coarse sediments due to fewer grain-grain contacts per unit volume, so that there are fewer constrictions through which oil must pass to penetrate more deeply.
- The larger void spaces between grains also mean that a larger volume of oil can enter and be stored in the material of a coarse-sediment beach.

Hayes and Michel (2001) described the features of gravel beaches that enhance oil persistence:

- High porosity and permeability that allow deep penetration from the surface.
- Potential for deep and rapid burial by clean sediments.
- Presence of localized, sheltered areas where oil can persist for years.
- Complex patterns of sediment reworking during storms.
- Slow rates of natural replenishment.

Bernabeu et al. (2006) studied the oil contamination of the inter-tidal area of two beaches impacted by heavy oil from the Prestige spill. The characteristics of the heavy oil would indicate a low capacity for penetration into sediment. However, oil was found embedded up to 2.38 meters and below the groundwater. The researchers concluded that the dynamic behaviour of the beach contributed to the burial of the oil in the sediment.

Guyomarch and Merlin (2000) conducted experiments on the weathering properties of several crude oil, including changes in oil adhesion with weathering. Oil adhesion was found to increase with weathering time, provided weathering is linked with oil viscosity.

8.1.3 Tank testing of spilled oil / sediment / sand interaction

An extensive body of work on the loading capacity, penetration, and retention of oil in coarse sediments has been carried out in a group of studies known as SOCS and SOCSEX (Subsurface Oil in Coarse Sediments Experiments).

Humphrey and Harper (1993) conducted a series of oil penetration and tidal flushing experiments in columns containing granules and pebbles. The development of the Stranded Oil in Coarse Sediment (SOCS) model was described by Humphrey, Owens, and Sergy (1993). Oil stranded on a beach penetrates only during the tidal period when that part of the beach is above the tidal level, so that penetration in the upper inter-tidal zone is expected to be greater than in the lower intertidal zone. For beaches made up of a mixture of gravel, the time required for penetration to more than a few centimetres may require more than one tidal cycle, especially if the oil is weathered or emulsified.

The emphasis of these studies was on the penetration of oil into the beach; the fate of oil remobilised off of the beach (probably containing some beach material) was not studied.

A series of experiments known as the "Stranded Oil in Coarse Sediments Experiments" (SOCSEX II) were conducted by Harper and Kory (1995). In these experiments, a variety of oils were applied to several sediment types to measure penetration and retention in vertical columns. The major conclusions of the study were:

- Penetration and retention of oil in sediments could not be related to any single oil property (viscosity, adhesion, wax content, etc.).
- The ability of oil to penetrate sediment is reduced with weathering and cooling of the oil.
- Heavy fuel oils penetrate coarse sediments more easily than most crude oils.
- Crude oils penetrate fine sediments more readily than fuel oils.
- For a given oil, the penetration increases with sediment coarseness.
- In fine sediments, penetration is sensitive to small changes in grain size.
- Oil retention is inversely related to penetration potential. Oils that penetrate sediments more easily have lower oil retention, whereas oils that are penetration-limited often have high oil retention.
- Oil retention in excess of 200 L/m³ (an oil-in-sediment content of $>10\%$ by weight) were documented.
- For a given oil, retention decreases in coarser sediments.
- Each oil shows unique retention patterns.
- Heavy fuel oils show maximum retention in coarse sands whereas crude oils show maximum retention in granules.

• Very small changes in grain size in mixed sediments can result in substantial changes in oil retention.

8.1.4 Modelling approaches to oil / sediment interaction

The basis for the mathematical model developed by Payne et al., 1987 and 1989 is the rate of reaction of oil droplets and SPM (Suspended Particulate Matter), and it is proportional to the concentration of each. The proportionality constants are the turbulent energy dissipation rate, the particle-particle sticking coefficient and geometric factors. Particle- particle kinetics was originally described by M. Smoluchowski (1917), and somewhat more recently, Birkner and Morgan (1968) presented an experimental study similar to the oil / SPM programme. The model used, not developed, for oil / SPM kinetics is essentially a well-known general particle-particle kinetics expression.

The oil droplet and SPM model considers oil droplets being dispersed into the water column from the surface and sediment being fluxed into the water column from the bottom. The oil droplets and SPM collide and stick to form SPM agglomerates at specific rate constants that are entered by the user.

One research team has developed models that describe OMA formation. Sterling et al. (2004) and Sterling et al. (2005) described a modelling approach that simulates changes in particle size distribution and density due to aggregation by extending the Smoluchowski aggregation kinetic model below to particles of different density:

Sterling et al. (2004) and Sterling et al. (2005) used a parameter estimation algorithm to estimate homogeneous collision efficiencies for single-particle type systems and heterogeneous collision efficiencies for two-particle systems. Homogeneous collision values were greater for clay (0.7) and for crude oil (0.3) than for silica (0.01). Clay and crude oil were classified as cohesive particles and silica was classified as non-cohesive. Heterogeneous collision efficiencies were similar for oil-clay (0.4) and oil-silica (0.3) systems.

Crude oil increases the aggregation of non-cohesive particles. Data were used to estimate firstorder flocculation rates, K' for oil, clay, and silica, and second-order rates, K" for oil and clay in oilclay systems. For oil or clay systems, clay aggregation and droplet coalescence can occur at the same relative time scales of clay settling and oil resurfacing. For mixed oil-clay systems, the relative time scales of clay settling and clay-oil aggregation were also within an order of magnitude. According to these researchers, oil-clay aggregation (or OMA formation) should be considered when modelling crude oil transport in nearshore waters.

Khelifa et al. (2005) conducted a laboratory study to validate the formation of oil-mineral aggregates (OMA) in cold brackish and sea waters. Chalk was found to form OMA better than bentonite. The in-situ sediment concentration that maximized oil dispersion was about 300 to 400 mg/l. Stabilization of about a 90% of Heidrun crude oil requires 300 mg/l of bentonite and 200 mg/l of chalk.

The oil spill model SIMAP (Version 4.3) (French McCay et al., 2004), developed by Applied Science Associates (ASA), wind data, current data, and transport and weathering algorithms to calculate the mass of oil components in various environmental compartments (water surface, shoreline, water column, atmosphere, sediments, etc.), oil pathway over time (trajectory), surface

oil distribution, and concentrations of the oil components in water and sediments. SIMAP uses the oil / SPM interaction model developed by Kirstein and Clary, 1989 based on the work carried out in Payne et al., 1987 and 1989. This algorithm is only used when the suspended sediment load is greater than 10 mg/l (French McCay et al., 2004).

Etkin et al., 2007 reviewed the state-of-the-art of modelling of the interactions between spilled oil and shorelines, but concluded:

"Despite the large body of published research on shoreline oiling, there remain significant information gaps with regard to the dynamic processes involved in shoreline oiling even over the relative short-term that would be most directly and practically applicable to oil spill risk analysis modelling."

Modelling of oil-shoreline interactions has been handled in a number of ways, including:

- Assuming all oil reaching a shoreline accumulates on that shore segment;
- Assuming all oil reaching a shoreline strands on the shore segment if the tide is receding;
- Using empirical data, relating the maximum amount of oil retained on shore to shore type and oil viscosity, to quantify a oil-holding capacity (e.g., Gundlach, 1987); and
- Utilizing a complex shoreline interaction model based on shore geography and hydraulic interactions (i.e., the COZOIL model developed by Applied Science Associates, Inc. for MMS: Reed et al., 1986, 1988, 1989; Gundlach, 1987; Coastal Science & Engineering, 1986, 1988; Reed and Gundlach, 1989a,b; and the surf zone oil transport model by Cheng et al., 2000).
- Using a statistical approach, i.e., a simple regression model to predict the lengths of coastline that would be impacted by an oil slick based on observational data from actual oil spills.

The simplest modelling approach is to accumulate oil on shore when floating oil reaches a shore segment, regardless of the oil type, weathering characteristics, shore type, amount of oil already on the shore, current and turbulence conditions, and so forth. Many models use this simplification. However, it might be desirable to incorporate some of the processes that result in some oil being re-mobilised from a shoreline.

As Etkin et al., 2007 note, a comprehensive review of literature on shoreline oiling emphasized that the behaviour of spilled oil, as it first becomes deposited or stranded on a shoreline, is complex and depends on a number of interrelated factors:

- The type and characteristics of the oil (e.g., viscosity);
- The thickness of oil already on the shoreline;
- Time until shoreline contact;
- Timing of the spill oil's arrival with regard to tides;
- Shoreline type;
- Weather at the time of and after the spill; and
- Wave energy at the shoreline.

Accumulation of oil on shore up to an empirically-derived oil-holding capacity is used by some oil spill models that include some kind of shore interaction algorithm (Gundlach and Reed, 1986; Gundlach, 1987; French et al., 1996; Reed et al., 1999, 2000; Cheng et al., 2000; French McCay, 2004.) The advantage of this approach is that it is simple to implement. However, considerable data are required to derive appropriate holding capacities.

Gundlach (1987), Gundlach and Reed (1986), and Reed et al. (1986) developed a computer-based model (SMEAR) representing oil-shoreline interactions.

Coastlines were identified as one of seven types based on ESI categories:

- Exposed rocky shores
- Sand beaches
- Gravel beaches
- Sheltered rocky shores
- Peat scarps
- Tidal flats
- Marshes/wetlands

Oil intersection a specific shoreline segment was determined by the transport model, which summed motions induced by wind and currents. Oil intersecting the shore was retained on-shore up to an empirically-derived oil-holding capacity. The oil-holding capacity data were derived from observations on moderately to heavily oiled beaches following the Amoco Cadiz, Urquiola, and Ixtoc I spills (Gundlach, 1987)

Once onshore, oil persistence was determined by tidal level and a removal coefficient for each shoreline type. Oil removal coefficients (Kf) were calculated from empirical data using the equation:

$$
M = M_{io} \cdot e^{-K_f t}
$$

Where
$$
Mi = \text{mass of oil on beach segment}
$$

$$
Mio = \text{mass of oil originally deposited on the beach}
$$

$$
K_f = \text{removal rate constant based on exponential decay}
$$

$$
t = \text{time in days since original deposition}
$$

Rate constants and removal rates are shown in Table 9.

Table 9. Rate constants and removal rates used in the SMEAR model (from Etkin et al., 2007)

Any interaction between the spilled oil and the shoreline substrate that results in some of the shoreline substrate becoming attached to the oil and subsequently sinking is not modelled by SMEAR.

The coastal zone oil spill model, COZOIL (Reed et al., 1986, 1988, 1989; Reed and Gundlach, 1989a,b; Howlett, 1998) is probably the most comprehensive model that includes a dynamic representation of processes controlling oil distribution in the coastal zone (Figure 35).

Figure 35. COZOIL Mass-Transfer Pathways in the Coastal Zone (From Reed, Gundlach, and Kana, 1989)

In COZOIL, the foreshore is the shoreline between mean low and high water (tidal range) and the backshore is the shoreline above mean high water. When oil comes ashore, if the tide is lower than the high tide level and the tide is receding, the oil is deposited if the foreshore has not already reached its oil-holding capacity for oil. If the water level is at or exceeds the mean high tide level, oil is deposited on the backshore by the waves (in the splash zone). The maximum holding thickness is a function of oil viscosity and shore type.

Inside the surf zone, entrained oil was represented as a continuous distribution, within individual alongshore grid cells. Incorporation of water into surface oil (emulsification) was simulated offshore and de-emulsification (de-watering) was allowed to occur for oil on the foreshore or backshore.

Oil coming ashore could be deposited on the foreshore or the backshore, or carried into coastal indentations (lagoons, ponds, or fjords). Each of the shore types in the COZOIL model were characterized by a unique set of parameters, including grain size, porosity, and a maximum oil thickness which the foreshore could retain. Oil on the foreshore penetrated into the underlying sediments at a rate dependent on sediment grain size and oil viscosity. Oil could also be carried into the beach groundwater system by wave overwash. Refloatation of surface oil occurred during rising tides.

The eight types of shorelines defined in the COZOIL model were:

- Smooth rocky shore or seawall
- Cobble beach
- Eroding peat scarps
- Sand beach
- Gravel beach
- Tidal (mud) flat
- Marsh
- Coastal pond, lagoon, or fjord

For each of the shore types, there are eight parameters required by the model:

- Reach length (m)
- Backshore width (m)
- Foreshore width (m)
- Offshore distance (m)
- Backshore slope (rise/run)
- Foreshore slope (rise/run)
- Offshore depth (m)
- Reach orientation

The COZOIL model requires a very large amount of site-specific input data and includes algorithms that are difficult to apply in other models and areas because the needed input data have not been compiled. It also does not include terms to describe the adherence of oil to shoreline substrate prior to remobilisation that could lead to the oil / substrate mixture sinking.

8.2 Detection techniques under development

Attempts to advance the potential of sonar sensors for sunken and submerged oil are being undertaken both in Europe and in the USA. In Europe following the Erika incident CEDRE undertook the Detection de Nappes Immergees (DENIM), and EXCAPI projects and these studies were continued and expanded under the wider European ASMA project (ASMA, 2007, Hansen, K et al 2008).

In the course of its studies, CEDRE evaluated 6 different sonar systems in the dry dock at Brest. Targets of 3-8cm in depth and 80 and 160cm diameter were provided using HFO, emulsified HFO and sediment mixed emulsified HFO. These experiments confirmed the difficulty of detection, resulting from the high attenuation of sonar signals by the sunken oil. Recommendations included the concept that wide area surveys with conventional side looking sonar would need to be supported, in order to address false targets, by more precise surveys, possibly using forward looking sonar, acoustic cameras or video systems.

In the USA, Kurt Hansen of the US Coastguard R&D Center has been leading a team to evaluate and develop sunken oil detection systems. This work has included testing and examination of a number of systems. Final results of the work have not yet been published but preliminary results were published at AMOP 2008.

Figure 36. Sunken oil Sonar Targets (photo courtesy of OHMSETT)

Two test oils were used: Sundex 8600 and No. 6 fuel oil. These were mixed at a rate of 35% with barite in order to ensure the oil remained on the bottom. Two test trays of 2.4 meters by 2.4 meters were constructed. The trays were filled with sand and geometric-shaped, vertical-sided depressions were created and 6 to 8 inches of oil inserted. The trays were placed in the OHMSETT test tank (Figure 36). The four systems were tested to proof of concept stage in clear water with low turbidity and no sediment covering. All systems detected targets under these test conditions.

The systems tested by the US Coastguard were:

- WHOI system (which combines a TETHYS mass spectrometer and UV fluorometer)
- The SAIC Modified Laser Line Scan System
- RESON sonar
- The EIC Fluorosensor

8.2.1 WHOI System

The WHOI detection system relies on two complementary modes of hydrocarbon sensing: a TETHYS mass spectrometer and a commercially available UV fluorometer. The TETHYS instrument is an underwater in-situ mass spectrometer developed through a partnership between the Woods Hole Oceanographic Institution and Monitor Instruments LLC. The UV fluorometer (Chelsea Instruments Ltd., Surrey, England) is sensitive to aromatic hydrocarbons fluorescing at 360 nm.

The tests identified a need to improve the system to optimise and improve the spectral resolution and sensitivity to the oil fractions identified in the fuel oil.

The WHOI system had already shown capability of detecting some oils in a calm water column. The system relies however on detection / presence of lighter components of the oil in the water column. It is not clear how much dissolved or particulate oil would be in the water column under field conditions or how long this would persist.

8.2.2 SAIC Modified Laser Line Scan System

The SAIC SM-2000 Laser Line Scan System (LLSS) was originally developed as a seafloor imaging tool based on the reflectance of a solid-state Nd-YAG 532 nm (blue-green) laser. In order to elicit fluorescence in oil-based compounds, a shorter wavelength, higher energy laser light source approaching the UV-A band (400 nm) was incorporated in the LLSS.

The system provided accurate imagery data pertaining to the shape and relative position of the various targets, but failed to elicit and/or detect any fluorescent signal over the background light.

The overall results of the tank testing indicated that the LLSS was primarily an imaging system in daylight conditions, detecting the ambient light and backscatter (noise). When ambient light levels decreased after sunset, the capabilities and potential of the modified LLSS in eliciting and recording fluorescence (signal) could be realized.

The SAIC system is adapted from an existing system and appears to work in low light conditions given reasonable clarity. Any future tests should take place in a more realistic environment so that the light levels and focal length are in line with the system performance, conditions that cannot be met in a controlled tank environment.

8.2.3 RESON 7125 SeaBat System Overview

The SeaBat 7125 system is a multibeam sonar system that measures relative water depths over a wide swath perpendicular to the vehicle's track. The system is suitable for mounting on a number of survey platforms.

All targets presented to the sonar were positively detected with a probability in excess of 80%. Extraction of the results required post-test processing but the manufacturer is already engaged in the development of more automated detection capabilities to supplement operator visual detect methods. This is anticipated to include use of advanced image processing programmes examining the backscattering strength.

RESON was found to have potential but the performance in field situations where the difference in density between the oil and bottom sediment is smaller remains to be assessed.

8.2.4 Particle size analyzer

This system, which makes use of laser systems, analyzes the deviation (diffraction) occurred to a light ray while passing through a small layer of water. Such deviation is directly proportional to the density and granulometry of the suspended particles. In this way the instrument is able to do a particle size distribution (PSD). The measure is independent from the particles composition. The deviation is recorded by a multi ring detector while the measure is known as "volume scattering function", which gives the granulometric distribution data through a mathematical process. Obviously every measure has to be integrated by means of other instruments able to check whether the observed particles effectively correspond to hydrocarbons. The instrument appears effective in precense of oil droplets dispersed along the water column.

8.2.5 EIC Fluorosensor

Fluorescence spectroscopy has been shown to be an effective tool for monitoring oil contaminants in water. Because the main constituents of oils are aromatic compounds, illumination of oil samples with ultraviolet or visible light causes the oil samples to emit fluorescence. Fluorescencebased methods have several advantages, including: they are non-contact, sensitive to the presence of aromatic hydrocarbons and easily miniaturized. There are, however, other fluorescing sources that may interfere with measurements.

OHMSETT test results indicate it is capable of accurately detecting heavy oil in real time. Oil targets in the test platforms showed significant fluorescence polarization signals and were easily distinguished from ambient backgrounds such as sunlight or background fluorescence. All testing was done during daylight hours.

The EIC equipment is a new approach and, while there are potential risks in the development, the small size of the equipment may lend its applications to multiple uses including mounting in small ROVs or autonomous vehicles or a suction head for recovery operations.

These two systems were determined to have the most promise for field use and, in particular, operation in low visibility conditions and against more representative targets. Development and testing of the other sensors and alternatives will also be permitted to developers and manufacturers (utilising the same test areas and targets established for the project) although the study itself will concentrate solely on these two systems.

8.2.6 Laser fluorosensors

Laser fluorosensor techniques have been developed and shown to be able to detect oil in the water column for the purposes of oil exploration (Dick and Fingas, 1992; Dick et al., 1992), though this is an expensive technique. Little evidence exists that this technique has been used in responding to spills of nonfloating oils, however (Brown et al., 1997). Laboratory experiments (Brown, 1998) have demonstrated a laser airborne fluorosensor that can detect the presence of dispersed bitumen in the water. No field tests or practical uses of the system have been made to date (National Research Council, 1999).

Laser fluorosensors exploit the capacity of some hydrocarbons to absorb ultraviolet light and become electronically excited. The absorbed energy is re-emitted as fluorescence, with emission of light in the visible spectrum. The time of decay for the light energy is in the range of 1-3,5 ns for crude oils (Figure 37) and 3,8-8 ns for refined products (Figure 38)(Pastayena *et al.*, 2000). Since only a few compounds present such behaviour, fluorescence usually provides a strong indication regarding the presence of oil within the water column. Many fluorosensors able to detect fuel oil spills operate in the UV spectrum, in the 300-355 nm region. With these frequencies natural fluorescent molecules, such as chlorophyll, emit light at sufficiently different wavelengths (685 nm) that their signal is not confused with the one of hydrocarbons. Furthermore, some organic compounds, known as yellow matter and normally present within the water column, emit a wide response BANDA centered at 420 nm. Their signal can often overlap the one coming from many crude oils, which varies between 400 and 650 nm with a peak at 480 nm. Generally crude oils show a characteristic displacement towards blue while refined products towards UV (Pastayena *et al.*, 2000).

By means of lasers a further signal is recorded, known as Raman scattering, due to the fact that energy is transferred from incidental light to water molecules. Water absorbs part of the energy as rotational and vibrational energy and emits light at a wavelength around 344 nm (this value is obtained when incidental light has a wavelength of 308nm). Raman scattering can prove to be very useful when estimating the thickness of the hydrocarbons layer; the oil, in fact, strongly absorbs the light and consequently the Raman signal is reduced, proportionally to the thickness of the oil. This system can be fully operational also during the night hours (Pastayena *et al.*, 2000, Brown *et al.*, 2002; Brown *et al.*, 2003).

8.2.7 Light detection and ranging system (LIDAR)

LIDAR is a recently developed laser system which makes use of the principle described previously and utilizes two other technologies at the same time: Global position System (GPS) and Inertial Navigation System (INS). This system enables to obtain accurate data even when the laser is positioned on a moving platform (airplane, ship, ecc).

SLEAF is the new generation of the Laser Environmental Airborne Fluorosensor (LEAF), which was developed in Canada in 1992. The original fluorosensor was able to illuminate an area only 10 centimetres wide and 30 centimetres long at an altitude of 100 metres, making it easy to miss spills on beaches and shorelines, where oil tends to pile up in a narrow band at the high tide line. The new sensor is equipped with a high-powered laser strong enough to operate at an altitude of 600 metres, giving it a field of view six times as large as that of LEAF. The laser beam is able to collect 400 samples per second in a swath up to 200 metres wide.

A LIDAR system has been evaluated through an experiment on field aimed at verifying its capacity to detect subsurface Orimulsion 400, present in small and variable quantities in a container filled up with water. The system has been positioned on an airplane flying at 81 m height with respect to the target. It is a Scanning Laser Environmental Airborne Fluorosensor (SLEAF) provided with a range gated detection system which allows the detector to turn itself on at the precise moment the

arrival of the signal at a certain depth is expected. In this way, is possible to exclude the signal deriving from the water surface, putting in evidence only the one related to the selected depth.

Figure 39 shows the progressive reduction of the yellow matter signal as long as the Orimulsion concentration is increased; at the same time the recorded spectrum becomes more similar to the spectrum of Orimulsion alone.

Figure 39 Emission spectra obtained during the experiment with SLEAF

Depending on water turbidity, the SLEAF system is able to work efficiently up to 3 meters of depth, being able to detect subsurface oils (Brown *et al.,* 2003).

The LIDAR system can also be mounted on a R.O.V. (Figure 40), useful to relieve oil along the water column.

Lidar fluorosensors were conceived to remotely measure phytoplankton content, to assess water quality parameters, to perform surveillance after ship accidents, to locate and detect the release of toxic chemicals and to inspect the seafloor, due to their capability of extracting signatures of dispersed (crude oils, phytoplankton) or dissolved substances (CDOM - Coloured Dissolved Organic Matter) from the laser induced fluorescence spectra. Since seawater optical characteristics limit the transmission of both the exciting laser beam and the generated fluorescence signal the instrument has been developed in order to be sent on a submersible carrier (an R.O.V.). By means of such a Lidar fluorosensor can provide a depth profiles of different substances concentration (dissolved organic substances, phytoplankton) and other seawater parameters can be extracted.

Figure 40 LIDAR system mounted on a R.O.V.

8.2.8 Sonar Multibeam

Sonar Multibeam hits the sea bottom by sound waves but output data are given as depth and not as image. As a matter of fact by such a method only the time that wave takes between transducer and bottom and return to detector is recorded.

The time recorded is transformed in bathymetrical data by means of the simple equation: wave speed=space (twice bathymetry)/ time elapsed.

Normally MB is fixed under the keel of the ship so coverage of the bottom depends on bathymetry, generally amounting to twice and four times depth.

A 3D bottom profile by different colours corresponding to different depth ranges is obtained; otherwise is possible to have a shadow effect as if bottom would be hit by sunlight (Figures 41 and 42).

Figure 41 Seafloor image from Side Scan Sonar

Figure 42 Same seafloor image from sonar Multibeam

8.2.9 Sub bottom profiler

Sub bottom profiler (SBP) systems deployment, both traditional and CHIRP technology, is possible to gain very high resolution seismic profiles.

The method detects acoustic contrasts of marine sediments layers (represented in seismic slices by reflecting levels, named reflectors); the resolution is of few cm close to the bottom. The method could be able to assess the acoustic contrast between water and bitumen oil (the top of polluting level) and between oil and "clean" sediments (bottom of polluting level).This is true whether oil

polluting deposit has a higher thickness width with respect to the resolution power of the device. Consequently the system is able to detect even oil layers covered by sediment, variably thick.

Another relevant factor is the knowledge of geometry of bitumen bottom coverage, in order to detect bitumen deposits along seismic slices.

Whether oil products are fluid they will deposit into morphological depressions. In this case, which is the most likely, is possible to detect these deposits onto sub bottom profiles featured by a concave surface trend.

The limit of the method is given by the slightest thickness of the bitumen deposit that can be detected. A digital SBP, with a high resolution power, is particularly suitable for this task. Data is acquired and then elaborated by a specific software for seismic signals, in order to increase the relation signal/noise.

In marine geology, SSS and SBP surveys are often carried out together, in order to acknowledge at the same time the superficial morphology of the bottom and the reflectors geometry underneath the surface: the same can be suggested here.

8.2.10 3D Multibeam sonar

This new technology is able to provide, by a single acoustic impulse (ultrasound), volumetric data regarding the water column investigated. It generates instantaneous images, and each image is based on only one acoustic transmitter pulse.

From two to ten images per second are acquired that matched together give a 3D acoustic film. In particular, it is possible to gain information regarding the position (latitude, longitude and depth) of each target and its reflecting strength. An important feature of this new technology is that it is real time. The investigated volume is a cone hit by acoustic energy. The energy reflected by any met obstacle is detected by a large number of hydrophones; each of them generates a 2D image. For each impulse a large number of 2D images is obtained, these are later processed resulting in a three-dimensional image. The detection range is 100-150 meters and can work with acoustic frequencies equal to 150, 300 and 600 kHz. The three frequencies offer 3 different resolutions/viewing angle alternatives. The system enables the operator to select freely his observation point in 3D, in order to observe the detected objects, to calculate the volume of the selected object and to determine the bottom morphology and bathymetry.

The above mentioned system could be very useful when trying to detect and monitor oil spills from wrecks or underwater pipelines and to detect suspended oil particles, irrespective of turbid water. Experiments on field evidenced the capacity of the system to detect gas bubbles emitted by a tube (Figure 43) at 6 meters of depth (Hansen, 2002a; Hansen, 2002b). Applied to gas leak detection, the most suitable frequency has proved to be 300 kHz which allows a column of leaking gas to be seen as a column and the vertical movement to be seen in real time.

Figure 43 3D acoustic sonar image of a gas leak observed from an underwater tube (source: Hansen, 2002a; Hansen, 2002b)

8.3 Recovery devices under development

The U.S Coast Guard R&D Center have embarked on a project to develop a complete approach for submerged oil recovery. In 2011 three companies were awarded contracts to build prototypes for testing – a submersible dredge, a manned submersible and a remotely operated vehicle system (Hansen 2011).

The Tornado Motion Technologies (TMT) OSBORS (Oil Stop Bottom Oil Recovery System) consists of a tracked seabed unit (generating a maximum ground pressure of 5 Psi) on which is mounted an eddy pump and a movable controllable suction head (Figure 44). The unit is designed for surface remote control using vehicle mounted cameras to identify targets. The unit also features GPS tracker system allowing it to be directed to targets fixed by other survey systems. The tracked system is reported to create less turbulence than conventional systems. The maximum working depth is in excess of 60m or as little as 30cm and recovery rates of 240 $m³/hr$ are quoted. The unit is designed to allow a diver operated "stinger" to be attached.

Figure 44 Tornado Motion tracked sunken oil recovery system

Marine Pollution Control Corporation (Detroit, MI) has developed a submerged oil recovery that utilises a pump-based recovery technology with a manned underwater vehicle/mini-submarine (US patent #7,597,811 – Canadian Patent Pending). The system allows for effective oil detection and recovery based on a logistic platform that completely avoids contact with the seabed and which places the trained recovery technicians at the recovery site. It incorporates RESON multi-beam oil-discriminating sonar (see section 8.2.3) and EIC Laboratories Florescence Polarisation (see section 8.2.5) to provide enhanced oil detection and oil mass survey capabilities. Recovery capacity is enhanced through the inclusion of a heated recovery nozzle system, and suction is provided by a submersible pump whose operation is directed by the submarine pilots who, using their visual vantage point and visual/audio/tactile sensors, are able to minimise run times when oil

is not present (increasing the overall yield of the recovery operation). This improved yield capacity was demonstrated at the OHMSETT test facility where a prototype of the pumping apparatus was successful in recovering high viscosity oil (+140,000 Cst) laden with sand from the bottom of the test tank.

Figure 45 MPC and SEAmagine Hydrospace Corporation sub sea oil recovery system

Alion have developed an ROV system called Sea Horse (Seagoing Adaptable Heavy Oil Recopvery SystEm). The recovery system consists of an ROV-powered sled, pump, nozzle and hoses. Sea View detection sonars form part of the detection component and the recovery system consists of two Sea Lion II ROVs, a Lamor GTA 20 pump and an aluminium framework (Figure 46).

Figure 46 Alion Sea Horse

Initial testing of these systems found that they meet most of the required specifications (Hansen 2011) for detection and recovery of submerged oil. These systems may not preclude the use of divers in some situations but divers may be substituted if the oil is deep (use manned submersible), in a surf zone (use crawler system) or if water is unsafe for divers (use ROV). Testing of these systems is ongoing and field tests are scheduled for later in 2012 (Hansen 2012).

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