



# FATE OF MARINE OIL SPILLS

TECHNICAL INFORMATION PAPER

2



# Introduction

When oil is spilled into the sea it undergoes a number of physical and chemical changes, some of which lead to its removal from the sea surface, while others cause it to persist. The fate of spilled oil in the marine environment depends upon factors such as the quantity spilled, the oil's initial physical and chemical characteristics, the prevailing climatic and sea conditions and whether the oil remains at sea or is washed ashore.

An understanding of the processes involved and how they interact to alter the nature, composition and behaviour of oil with time is fundamental to all aspects of oil spill response. It may, for example, be possible to predict with confidence that oil will not reach vulnerable resources due to natural dissipation, so that clean-up operations will not be necessary. When an active response is required, the type of oil and its probable behaviour will determine which response options are likely to be most effective.

This paper describes the combined effects of the various natural processes acting on spilled oil, collectively known as 'weathering'. Factors which determine whether or not the oil is likely to persist in the marine environment are considered together with the implications for response operations. The fate of oil spilled in the marine environment has important implications for all aspects of a response and, consequently, this paper should be read in conjunction with others in this series of Technical Information Papers.

## Properties of oil

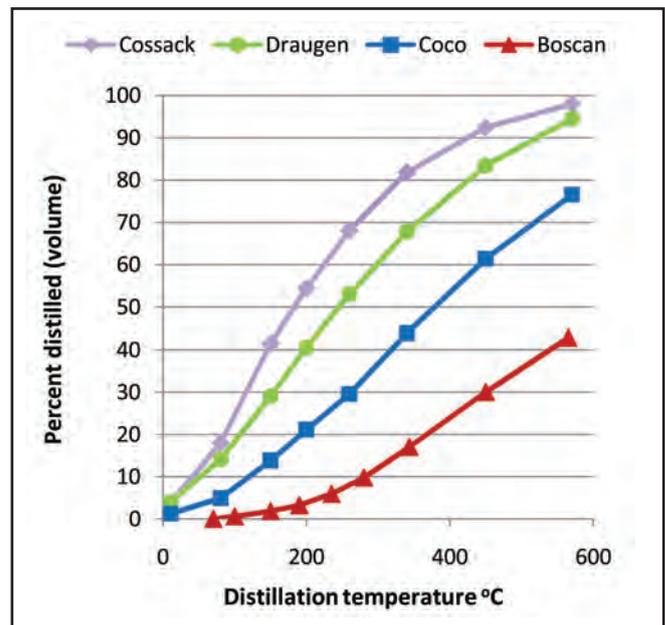
Crude oils of different origin vary widely in their physical and chemical properties, whereas many refined products tend to have well-defined properties irrespective of the crude oil from which they are derived. Intermediate and heavy fuel oils, which contain varying proportions of the residues of the refining process blended with lighter refined products, also vary considerably in their properties.

The main physical properties that affect the behaviour and the persistence of an oil spilled at sea are specific gravity, distillation characteristics, vapour pressure, viscosity and pour point. All are dependent on chemical composition, such as the proportion of volatile components and the content of asphaltenes, resins and waxes.

The **specific gravity or relative density** of an oil is its density in relation to pure water, which has a specific gravity of 1. Most oils are less dense or lighter than sea water which typically has a specific gravity of about 1.025. The American Petroleum Institute gravity scale, °API, is commonly used to describe the specific gravity of crude oils and petroleum products as follows:

$$^{\circ}\text{API} = \frac{141.5}{\text{specific gravity}} - 131.5$$

In addition to determining whether or not the oil will float, the specific gravity can also give a general indication of other properties of the oil. For example, oils with a low specific gravity (high °API) tend to contain a high proportion of volatile components and to be of low viscosity.

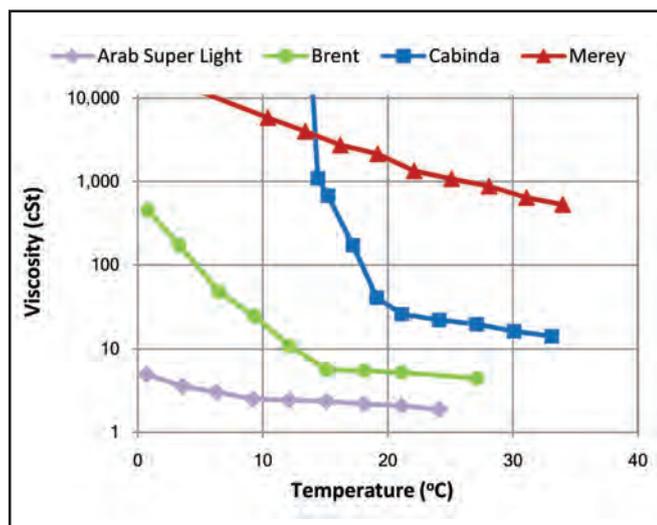


▲ Figure 1: Distillation curves for four crude oils. Oil remaining above the maximum temperature shown is primarily residue. Data from crude oil assays.

The **distillation characteristics** of an oil describe its volatility. In the distillation process, as the temperature of an oil is raised, different components reach their boiling point in succession, evaporate and are then cooled and condense. The distillation characteristics are expressed as the proportions of the parent oil that distil within given temperature ranges (Figure 1). Some oils contain bituminous, waxy or asphaltenic residues, which do not readily distil even at high temperatures and are also likely to persist in

	Group 1	Group 2	Group 3	Group 4
	Arabian Super Light	Brent	Cabinda	Merey
Origin	Saudi Arabia	UK	Angola	Venezuela
°API	50.7	37.9	32.5	17.3
SG at 15°C	0.79	0.83	0.86	0.96
Wax content	12%	No data	10.4%	10%
Asphaltenes	7%	0.5	0.16	9%
Pour point	-39°C	-3°C	12°C	-21°C

▲ Table 1: Physical characteristics of four typical crude oils. The colours and groupings correspond to the classifications in Table 2 (page 8).



▲ Figure 2: Viscosity/temperature relationship for the four crude oils in Table 1.

the marine environment for extended periods (e.g. Boscan crude in Figure 1).

The **vapour pressure** provides a further indication of the volatility of an oil, usually quoted as Reid Vapour Pressure measured at 100°F (37.8°C). A vapour pressure greater than 3 kPa (23mmHg) is the criteria for evaporation to occur under most conditions. Above 100 kPa (760mmHg), the substance behaves like a gas. Gasoline, for example, has a vapour pressure of between 40–80 kPa (300–600mmHg). Cossack crude has a Reid Vapour Pressure of 44 kPa and is very volatile with a high proportion of components boiling at low temperatures whereas Boscan crude is far less volatile with a Reid Vapour Pressure of just 1.7 kPa.

The **viscosity** of an oil is its resistance to flow. High viscosity oils flow less easily than those of lower viscosity. All oils become more viscous (i.e. flow less readily) as the temperature falls, some more than others depending on their composition. The temperature-viscosity relationships for four crude oils are shown in Figure 2. Units of kinematic viscosity\* are used in this paper, expressed as centistokes (cSt = mm<sup>2</sup> s<sup>-1</sup>).

The **pour point** is the temperature below which an oil no longer flows and is a function of its wax and asphaltene content. On cooling, an oil will reach a temperature, termed



▲ Figure 3: Oils spilled into the sea at temperatures below their pour point form semi-solid fragments. This image shows Nile Blend crude, pour point +33°C, in sea water of 28°C. Such oils are highly persistent and may travel great distances.

the **cloud point**, when the wax components begin to form crystalline structures. Crystal formation increasingly hinders the flow of the oil until on further cooling the pour point is reached, flow ceases and the oil changes from a liquid to a semi-solid (Figure 3). An example of this behaviour is shown for Cabinda crude oil in Figure 2. As this oil cools from 30°C the viscosity rises slowly but once below its cloud point of 20°C it begins to thicken exponentially. At the pour point of 12°C the viscosity has increased sufficiently to prevent flow.

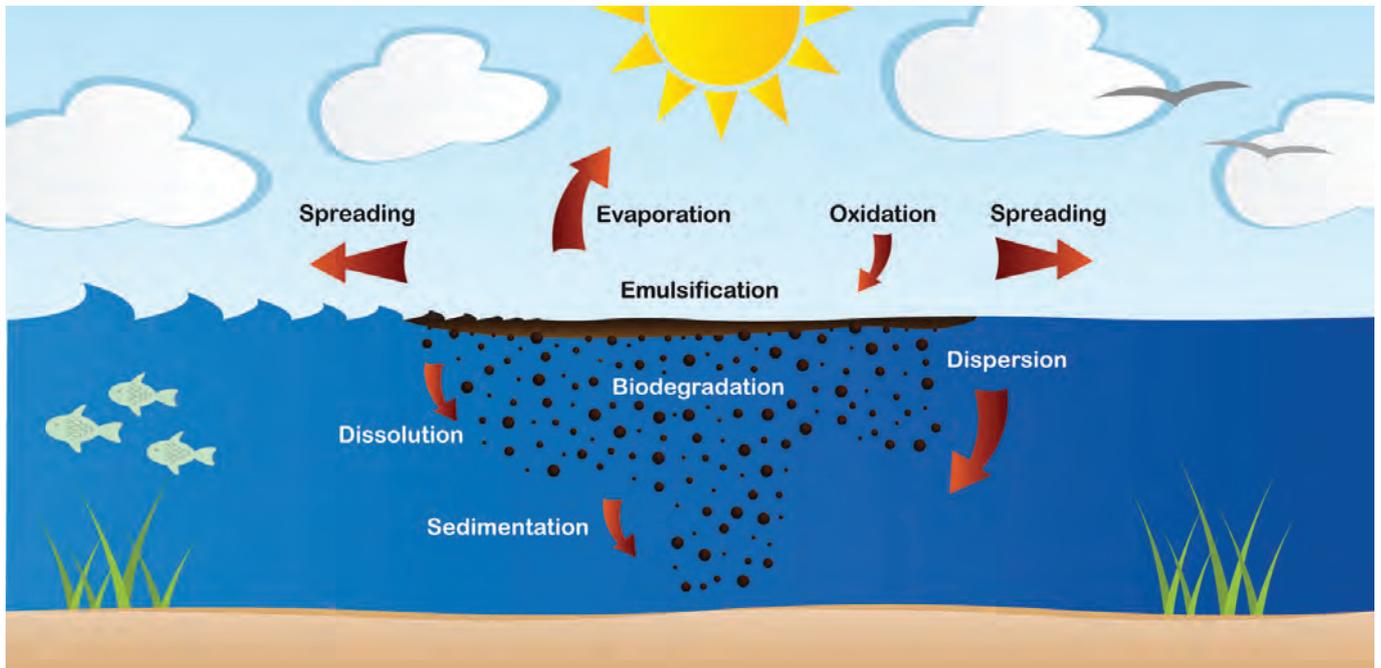
## Weathering processes

The individual processes discussed in the following section act together to bring about the weathering of a spilled oil (Figure 4). However, the relative importance of each process varies with time. This is illustrated in Figure 6 for a spill of a typical medium crude oil under moderate sea conditions. In addition to these processes, an oil slick will drift according to the wind and currents as described in the separate paper on Aerial Observation of Marine Oil Spills.

## Spreading

As soon as oil is spilled, it immediately starts to spread over the sea surface. The speed at which this takes place depends to a great extent on the viscosity of the oil and the volume spilled. Fluid, low viscosity oils spread much faster than those with high viscosity. Liquid oils initially spread as a coherent slick but quickly begin to break up. As the oil spreads and the thickness reduces, its appearance changes from the black or dark brown colouration of thick oil patches to iridescent and silver sheen at the edges of the slick (Figure 5). Rather than spreading as thin layers, semi-solid or highly viscous oils fragment into patches which move apart and may sometimes be centimetres thick. In open water, wind circulation patterns tend to cause oil to form narrow bands or 'windrows' parallel to the wind direction and, over time,

\* kinematic viscosity = dynamic viscosity ÷ density. Dynamic viscosity is measured in centipoise (cP) or SI equivalent millipascals per second (mPa s)



▲ Figure 4: Weathering processes acting on oil at sea. Once oil strands on the shoreline some of these processes will no longer apply.

the oil properties become less important in determining slick movement.

The rate at which oil spreads or fragments is also affected by waves, turbulence, tidal streams and currents – the stronger the combined forces, the faster the process. There are many examples of oil spreading over several square kilometres in just a few hours and over several hundreds of square kilometres within a few days. Except in the case of small spills of low viscosity oils, spreading is not uniform and large variations of oil thickness can occur, from less than a micrometre to several millimetres or more.

## Evaporation

The more volatile components of an oil will evaporate to the atmosphere. The rate of evaporation depends on ambient temperatures and wind speed. In general those oil components with a boiling point below 200°C will evaporate

within a period of 24 hours in temperate conditions. The greater the proportion of components with low boiling points, as shown by the oil's distillation characteristics, the greater the degree of evaporation. In Figure 1, for example, for Cossack crude, 55% of the crude is formed of components boiling below 200°C whereas for Boscan crude it is just 4%.

The initial spreading rate of the oil also affects the rate of evaporation since the larger the surface area, the faster light components will evaporate. Rough seas, high wind speeds and warm temperatures also increase evaporation.

Residues of the oil remaining after evaporation have increased density and viscosity, which affects subsequent weathering processes as well as clean-up techniques.

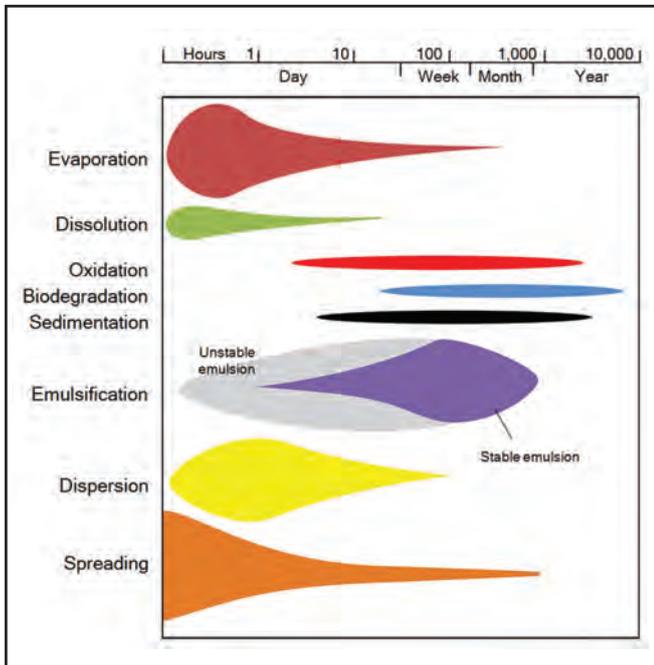
Spills of refined products, such as kerosene and gasoline, may evaporate completely within a few hours and light crudes, such as Cossack, can lose more than 50% of their volume during the first day. When such extremely volatile oils are spilled in confined areas, there may be a risk of fire and explosion or human health hazards. In contrast, heavy fuel oils undergo little, if any, evaporation and pose minimal risk of explosion. Nevertheless, heavy fuel oils can pose a fire risk. If debris is ignited in a pool of oil in calm conditions, it can form a wick sufficient to sustain a vigorous fuel oil fire.

## Dispersion

The rate of dispersion is largely dependent upon the nature of the oil and the sea state, proceeding most rapidly with low viscosity oils in the presence of breaking waves. Waves and turbulence at the sea surface can cause all or part of a slick to break up into droplets of varying sizes which become mixed into the upper layers of the water column. Smaller droplets remain in suspension while the larger ones rise back to the surface where they either coalesce with other droplets to reform a slick or spread out in a very thin film. For those



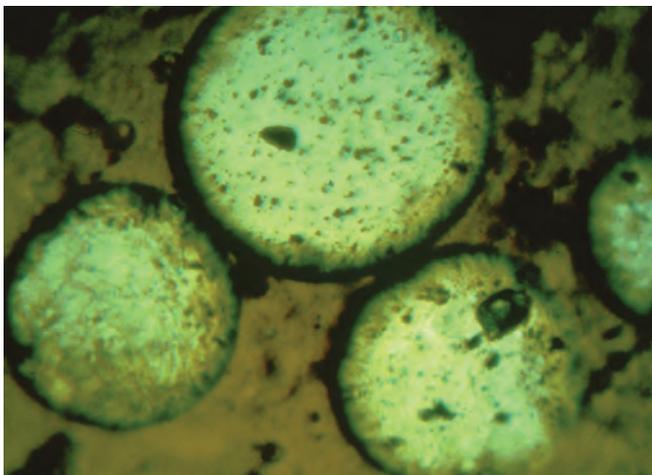
▲ Figure 5: When medium and light oils spread unhindered, very thin films eventually form. These appear as iridescent (rainbow) and silver sheens, which dissipate rapidly.



▲ Figure 6: A schematic representation of the fate of a typical Group 2/3 crude oil spill showing changes in the relative importance of weathering processes with time - the width of each band indicates the importance of the process (after a diagram courtesy of SINTEF).

droplets smaller than about 70µm in diameter, the speed with which they rise towards the surface is balanced by the turbulence of the sea so that they are held in suspension. This dispersed oil mixes into ever greater volumes of sea water, resulting in the rapid and very substantial reduction of the oil concentration. The increased surface area presented by dispersed oil also promotes processes such as biodegradation, dissolution and sedimentation.

Oils that remain fluid and spread unhindered by other weathering processes may disperse completely within a few days in moderate sea conditions. The application of dispersants can speed up this natural process. Conversely, viscous oils tend to form thick fragments on the water surface that show little tendency to disperse, even with the addition of dispersants.



▲ Figure 7: A greatly magnified image (x1,000) of a water-in-oil emulsion showing individual water droplets surrounded by oil.

## Emulsification

Many oils take up water and form water-in-oil emulsions. This can increase the volume of pollutant by a factor of up to five times. Emulsions form most readily for oils which, when spilled, have a combined Nickel/Vanadium concentration greater than 15ppm or an asphaltene content in excess of 0.5%. The presence of these compounds and sea states typically greater than Beaufort Force 3 (wind speed 3–5ms<sup>-1</sup> or 7–10 knots) determine the rate at which emulsions form. Viscous oils, such as heavy fuel oils, tend to take up water more slowly than more fluid oils. As the emulsion develops, the movement of the oil in the waves causes the droplets of water which have been taken up in the oil to decrease in size (Figure 7), making the emulsion progressively more viscous. At the same time, the asphaltene compounds can precipitate from the oil to coat the water droplets increasing the stability of the emulsion. As the amount of water incorporated increases, the density of the emulsion approaches that of sea water but, without the addition of solid particulates, is unlikely to surpass it. Stable emulsions may contain as much as 70% – 80% water, are often semi-solid, and have a strong red/brown, orange or yellow colour (Figure 8). They are highly persistent and may remain emulsified indefinitely. Less stable emulsions may separate into oil and water if heated by sunlight under calm conditions or when stranded on shorelines.

Formation of water-in-oil emulsions reduces the rate of other weathering processes and is the main reason for the persistence of light and medium crude oils on the sea surface and shoreline. Although stable water-in-oil emulsions behave similarly to viscous oils, differences in their compositions have implications for effective response options.

## Dissolution

The rate and extent to which an oil dissolves depends upon its composition, spreading, the water temperature, turbulence and degree of dispersion. The heavy components of crude oil are virtually insoluble in sea water whereas lighter compounds, particularly aromatic hydrocarbons such as benzene and toluene, are slightly soluble. However, these compounds are also the most volatile and are lost



▲ Figure 8: Recovery of emulsified heavy fuel oil showing a typical red/brown colour. Analysis showed the water content of the emulsion to be as much as 50%.

very rapidly by evaporation, typically 10 to 1,000 times faster than they dissolve. As a result, concentrations of dissolved hydrocarbons in sea water rarely exceed 1 ppm and dissolution does not make a significant contribution to the removal of oil from the sea surface.

## Photo-oxidation

Hydrocarbons can react with oxygen, which may either lead to the formation of soluble products or persistent tars. Oxidation is promoted by sunlight and, although it occurs for the entire duration of the spill, its overall effect on dissipation is minor compared to that of other weathering processes. Even under intense sunlight, thin oil films break down only slowly, and usually at less than 0.1% per day. Thick layers of very viscous oils or water-in-oil emulsions tend to oxidise to persistent residues rather than degrade, as higher molecular weight compounds are formed that create a protective surface layer. This can be seen in tarballs stranding on shorelines which usually consist of a solid outer crust of oxidised oil and sediment particles, surrounding a softer, less weathered interior.

## Sedimentation and sinking

Dispersed oil droplets can interact with sediment particles and organic matter suspended in the water column so that the droplets become dense enough to sink slowly to the sea bed. Shallow coastal areas and the waters of river mouths and estuaries are often laden with suspended solids that can bind with dispersed oil droplets, thereby providing favourable conditions for sedimentation of oily particles. In brackish water, where fresh water from rivers lowers the salinity of sea water and therefore its specific gravity, neutrally buoyant droplets of oil may sink. Oil may also be ingested by planktonic organisms and incorporated into faecal pellets which subsequently drop to the seabed. In rare instances, oil can become entrained with high levels of suspended solids during storm conditions and fall to the seabed. Similarly, wind-blown sand may sometimes be deposited on top of floating oil and cause it to sink.

Most oils have sufficiently low specific gravities to remain afloat unless they interact with and attach to more dense materials. However, some heavy crude oils, most heavy fuel oils and water-in-oil emulsions have specific gravities close to that of sea water and even minimal interaction with sediment can be sufficient to cause sinking. Only a very few residual oils have specific gravities greater than sea water ( $>1.025$ ), thereby causing them to sink once spilled.

Some oils can sink following a fire, which not only consumes the lighter components but also results in the formation of heavier pyrogenic products as a consequence of the associated high temperatures. This is a consideration if deliberate in-situ burning is contemplated as a response technique.

In rough seas, dense oils can be over-washed and spend a considerable amount of time just below the surface, making observation of oil from the air very difficult. This phenomenon is sometimes confused with oil sinking but when conditions become calm, the oil resurfaces.



▲ *Figure 9: Manual recovery of sunken heavy fuel oil.*

Sedimentation is one of the key long term processes leading to the accumulation of spilled oil in the marine environment. However, sinking of bulk oil is only rarely observed other than in shallow water, close to shore, primarily as a result of shoreline interaction (*Figure 9*).

## Shoreline interaction

The interaction of stranded oil with shorelines depends primarily on the levels of energy to which the shoreline is exposed and the nature and size of the shoreline substrate.

Sediment interaction leading to sinking most often results from oil stranding on sand shorelines. On exposed sand beaches, seasonal cycles of sediment build-up (accretion) and erosion may cause oil layers to be successively buried and uncovered. Even on less exposed sand beaches, stranded oil can become covered by wind-blown sand. Once oil has mixed with sand, it will sink if it is washed back into near-shore waters by tidal rise and fall or storms. A repetitive cycle often occurs whereby the oil/sand mixture is washed off the beach into near-shore waters and the coarser sand particles are released allowing the oil to float back to the surface. This oil then becomes stranded again to mix with the sand and the cycle repeats itself. A sheen emanating from a sand beach may be an indication that this process is occurring.

The interaction of the oil with very fine ( $<4$  microns) mineral particles (fines) within the shoreline leads to the formation of mineral- or clay-oil flocculates. Dependent on the viscosity of the oil, sufficient water movement can cause oil droplets to form to which the fines are electrostatically attracted. The fines surrounding the droplet prevent coalescence to larger droplets and adherence to larger sediment substrates, for example, sand or pebbles. The resulting stable flocculates are close to neutrally buoyant and small enough to be held in suspension by turbulence as water washes over the beach as a result of tides or storms. They can eventually become widely dispersed in coastal currents and, over a period of time, can account for the removal of much of the oil from sheltered (low energy) shorelines, where wave action and currents are too weak for other processes, for

example sediment abrasion, to occur.

Muddy sediments and marshes are common on sheltered shorelines. Under most circumstances the oil does not penetrate into these fine sediments and remains on the surface. However, 'bioturbation', the reworking of sediments by burrowing animals, sometimes allows less viscous oils to penetrate a little way into the sediment through migration of the oil down worm holes, plant stems and the like. Oil can also become incorporated into these fine-grained sediments during severe storm conditions when the fine mud particles are suspended in the water column and become mixed with oil. As conditions calm, the mud settles and the oil can become locked into the sediment. In these sheltered locations the sediment may remain undisturbed for lengthy periods. Since oxygen levels in the sediment are low, very little degradation will occur.

On sheltered shingle or pebble shorelines, high viscosity oils, if not removed during clean-up operations, can form 'asphalt pavements', primarily as a result of oxidation of the surface oil layer (*Figure 10*). Floating oil can penetrate these open substrates more readily and is then protected from removal by the sea and other weathering processes by the substrate itself. Asphalt pavements can persist for several decades if left undisturbed.

## Biodegradation

Sea water contains a range of marine micro-organisms capable of metabolising oil compounds. They include bacteria, moulds, yeasts, fungi, unicellular algae and protozoa, which can utilise oil as a source of carbon and energy. Such organisms are distributed widely throughout the world's oceans although they are more abundant in areas with natural seeps of oil or chronically polluted coastal waters, typically those close to urban centres which receive industrial discharges and untreated sewage.

The main factors affecting the rate and extent of biodegradation are the characteristics of the oil, the availability



▲ *Figure 10: As part of an experiment following a release of crude oil, an area of affected shoreline was deliberately left untouched. This patch of oil, approximately 1m<sup>2</sup>, remains after more than 15 years as asphalt pavement.*

of oxygen and nutrients (principally compounds of nitrogen and phosphorus) and temperature. A number of intermediate compounds are produced as the hydrocarbons are broken down but the eventual products of biodegradation are carbon dioxide and water.

Each type of micro-organism involved in the process tends to degrade a specific group of hydrocarbons and thus a wide range of micro-organisms, acting together or in succession, are needed for degradation to continue. As degradation proceeds, a complex community of micro-organisms develops. The micro-organisms necessary for biodegradation are present in relatively small numbers away from coasts in the open sea but multiply rapidly when oil is available and degradation will continue until the process is limited by nutrient or oxygen deficiency. In addition, although micro-organisms are capable of degrading many of the compounds in crude oil, some large and complex molecules are resistant to attack and these residues tend to include the compounds which give oil its black colour.

Products intended to enhance the rate of biodegradation are available. The efficacy of such materials is questionable since it is unlikely nutrients will be in short supply, especially in coastal waters and little can be done to increase oxygen levels or the water temperature.

The micro-organisms live in the water, from which they obtain oxygen and essential nutrients and, consequently, biodegradation can only take place at an oil/water interface. At sea, the creation of oil droplets, either through natural or chemical dispersion, increases the interfacial area available for biological activity, so enhancing degradation. In contrast, oil stranded in thick layers on shorelines or above the high water mark will have a limited surface area and very restricted contact with water. Under these conditions biodegradation will proceed extremely slowly, causing the oil to persist for many years if not removed.

The variety of factors influencing biodegradation makes it difficult to predict the rate at which an oil may be removed. Although biodegradation is clearly not capable of removing bulk oil accumulations, it is one of the main long term mechanisms for the natural removal of the final traces of oil from shorelines that are frequently over-washed by tidal or wind-driven sea movement.

## Combined processes

The combined effect of the processes described previously is summarised in *Figure 13*. All come into play as soon as oil is spilled, although their relative importance varies with time, as shown in *Figure 6*. Spreading, evaporation, dispersion, emulsification and dissolution are most important during the early stages of a spill, while photo-oxidation, sedimentation and biodegradation are longer-term processes that determine the ultimate fate of oil. Dispersion and emulsification are competing processes, with dispersion removing oil from the sea surface, while emulsification causes the volume of pollutant to increase and to persist. The factors that determine whether the oil will disperse or emulsify include: the release conditions (rate and amount spilled; surface or underwater

## Group 1 oils

- A:** °API > 45 (Specific gravity < 0.8)  
**B:** Pour point °C  
**C:** Viscosity @ 10–20°C: less than 3 CSt  
**D:** % boiling below 200°C: greater than 50%  
**E:** % boiling above 370°C: between 20 and 0%

	A	B	C	D	E
Asgard	49	-28	2 @ 10°C	58	14
Arabian Super Light	51	-39	2 @ 20°C		
Cossack	48	-18	2 @ 20°C	51	18
Curlew	47	-13	2 @ 20°C	57	17
F3 Condensate	54	<-63	1 @ 10°C	81	0
Gippsland	52	-13	1.5 @ 20°C	63	8
Hidra	52	-62	2.5 @ 10°C	60	11
Terengganu condensate	73	-36	0.5 @ 20°C	>95	0
Wolylbutt	49	-53	2 @ 20°C	55	4
Gasoline	58		0.5 @ 15°C	100	0
Kerosene	45	-55	2 @ 15°C	50	0
Naptha	55		0.5 @ 15°C	100	0

## Group 2 oils

- A:** °API 35–45 (Specific gravity 0.8–0.85)  
**B:** Pour point °C  
**C:** Viscosity @ 10–20°C: between 4 Cst and semi-solid  
**D:** % boiling below 200°C: between 20 and 50%  
**E:** % boiling above 370°C: between 15 and 50%

### Low pour point <6°C

	A	B	C	D	E
Arabian Extra Light	38	-30	3 @ 15°C	26	39
Azeri	37	-3	8 @ 20°C	29	46
Brent	38	-3	7 @ 10°C	37	33
Draugen	40	-15	4 @ 20°C	37	32
Dukhan	41	-49	9 @ 15°C	36	33
Liverpool Bay	45	-21	4 @ 20°C	42	28
Sokol (Sakhalin)	37	-27	4 @ 20°C	45	21
Rio Negro	35	-5	23 @ 10°C	29	41
Umm Shaif	37	-24	10 @ 10°C	34	31
Zakum	40	-24	6 @ 10°C	36	33
Marine Gas oil (MGO)	37	-3	5 @ 15°C		

### High pour point >5°C

	A	B	C	D	E
Amna	36	19	Semi-solid	25	30
Beatrice	38	18	32 @ 15°C	25	35
Bintulu	37	19	Semi-solid	24	34
Escravos	34	10	9 @ 15°C	35	15
Sarir	38	24	Semi-solid	24	39
Statfjord	40	6	7 @ 10°C	38	32

Note: High pour point oils only behave as Group 2 at ambient temperatures above their pour point. Below this treat as Group 4 oils.

## Group 3 oils

- A:** °API 17.5–35 (Specific gravity 0.85–0.95)  
**B:** Pour point °C  
**C:** Viscosity @ 10–20°C: between 8 CSt and semi solid  
**D:** % boiling below 200°C: between 10 and 35%  
**E:** % boiling above 370°C: between 30 and 65%

### Low pour point <6°C

	A	B	C	D	E
Alaska North Slope	28	-18	32 @ 15°C	32	41
Arabian Heavy	28	-40	55 @ 15°C	21	56
Arabian Medium	30	-21	25 @ 15°C	22	51
Arabian Light	33	-40	14 @ 15°C	25	45
Bonny Light	35	-11	25 @ 15°C	26	30
Iranian Heavy	31	-36	25 @ 15°C	24	48
Iranian Light	34	-32	15 @ 15°C	26	43
Khafji	28	-57	80 @ 15°C	21	55
Sirri	33	-12	18 @ 10°C	32	38
Thunder Horse	35	-27	10 @ 10°C	32	39
Tia Juana Light	32	-42	500 @ 15°C	24	45
Troll	33	-9	14 @ 10°C	24	35
IFO 180	18–20	10–30	1,500–3,000 @ 15°C		–

### High pour point >5°C

	A	B	C	D	E
Cabinda	33	12	Semi-solid	18	56
Coco	32	21	Semi-solid	21	46
Gamba	31	23	Semi-solid	11	54
Mandji	30	9	70 @ 15°C	21	53
Minas	35	18	Semi-solid	15	58

Note: High pour point oils only behave as Group 3 at ambient temperatures above their pour point. Below this treat as Group 4 oils.

## Group 4 oils

- A:** °API <17.5 (Specific gravity >0.95) or  
**B:** Pour point >30°C  
**C:** Viscosity @ 10–20°C: between 1500 CSt and semi-solid  
**D:** % boiling below 200°C: less than 25%  
**E:** % boiling above 370°C: greater than 30%

	A	B	C	D	E
Bachaquero 17	16	-29	5,000 @ 15°C	10	60
Boscan	10	15	Semi-solid	4	80
Cinta	33	43	Semi-solid	10	54
Handil	33	35	Semi-solid	23	33
Merey	17	-21	7,000 @ 15°C	7	70
Nile Blend	34	33	Semi-solid	13	59
Pilon	14	-3	Semi-solid	2	92
Shengli	24	21	Semi-solid	9	70
Taching	31	35	Semi-solid	12	49
Tia Juana Pesado	12	-1	Semi-solid	3	78
Widuri	33	46	Semi-solid	7	70
IFO 380	11–15	10–30	5,000–30,000 @ 15°C		

▲ Table 2: Example oils classified according to their °API (American Petroleum Institute gravity). The colours of each group relate to Table 1 and to Figures 1, 2, 12 and 13. Generally, persistence when spilled increases with group number.



▲ *Figure 11: A very heavy fuel oil on the seabed following its release from a damaged barge. The oil had an °API of 4, translating into a specific gravity of 1.04, compared to seawater of 1.025 (image courtesy of NOAA).*

release, etc.); the environmental conditions (temperature, sea-state, currents, etc.); and the physical and chemical properties of the oil.

An understanding of the way in which weathering processes interact is important when attempting to forecast the changing characteristics of an oil during the lifetime of a slick at sea. Predictions of potential changes in oil characteristics with time allow an assessment to be made of the likely persistence of spilled oil and thereby the most appropriate response option. In this latter regard, a distinction is frequently made between non-persistent oils, which because of their volatile nature and low viscosity tend to disappear rapidly from the sea surface, and persistent oils, which dissipate more slowly and usually require a clean-up response. Examples of the former are gasoline, naphtha and kerosene, whereas most crude oils, intermediate and heavy fuel oils, and bitumen are classed as persistent.\*

An alternative classification allocates commonly transported oils into four groups according to their °API (Table 2). The purpose of this is to group oils which are likely to behave in a similar way if spilled at sea. As a general rule, the higher the °API of the oil (and the lower the specific gravity), the less persistent it will be. It is important to appreciate, however, that some apparently light oils behave more like heavy ones due to the presence of waxes. Oils with wax contents greater than about 10% tend to have high pour points and if the ambient temperature is low, the oil will be either a semi-solid or a highly viscous liquid and the natural weathering processes will be slow.

\* *The international liability and compensation regime for tanker spills differentiates between persistent and non-persistent oils, the latter being defined as consisting of hydrocarbon fractions, (a) at least 50% of which, by volume, distills at a temperature of 340°C, and (b) at least 95% of which distills at a temperature of 370°C, when tested by the ASTM Method D 86/78 or any subsequent revision thereof.*

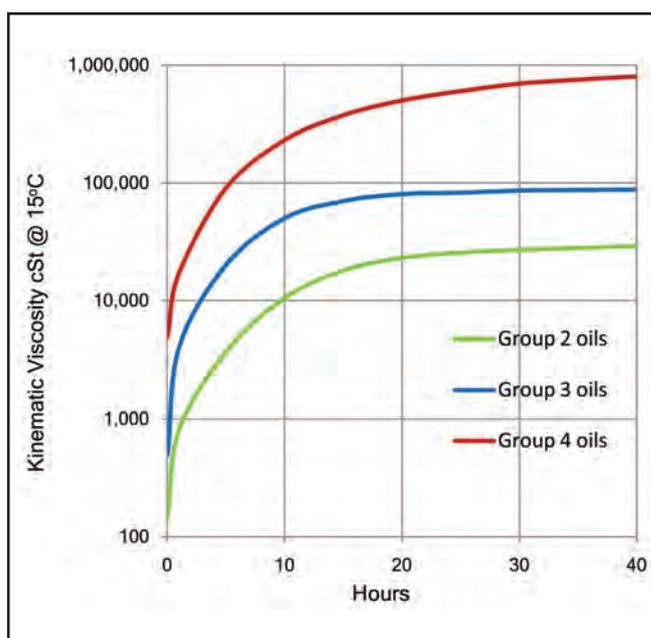
A fifth group is sometimes recognised for oils which have a specific gravity greater than 1 and °API less than 10. Such oils are likely to sink, particularly in brackish water, and are sometimes termed LAPIOs (Low API Oils). This category comprises very heavy fuel oils and residual slurry oils (Figure 11).

Figure 12 shows typical increases in viscosity with time after spillage for Groups 2–4 as a result of evaporation and emulsification, demonstrating that emulsification has the largest effect on the increase in viscosity.

Figure 13 shows a simplified schematic of the rate of natural removal of the four oil groups and also takes into account the effect of the formation of water-in-oil emulsions on the volume of pollutant over time. The schematic has been developed on the basis of observations made in the field and is intended to give an impression of how persistence varies according to the physical properties of the oil. The precise behaviour of an individual crude oil will depend on its properties and the circumstances at the time of the spill. Weather and climatic conditions will particularly influence the persistence of a slick. For example, in very rough weather an oil in Group 3 may dissipate within a time scale more typical of a Group 2 oil. Conversely, in cold, calm conditions it may approach the persistence of Group 4 oils. Group 4 oils, including heavy fuel oils which are carried as bunker fuel by many ships, are typically highly viscous and highly persistent, and are among the most problematic to clean-up. Their persistence gives them the potential to travel considerable distances at sea and to cause widespread contamination.

## Computer models

A number of computer models are available that forecast the movement or trajectory of an oil spill. Some include weathering predictions showing how spilled oil is likely to change with time under given sets of conditions. These often draw on



▲ *Figure 12: Typical rates of viscosity increase in moderate to rough seas. The viscosity of Group 1 oils never exceeds 100cSt in the marine environment and so is not shown.*

databases of the physical and chemical characteristics of different oils, as well as the results of scientific research and observations of oil behaviour. However, due to the complexity of the weathering processes and uncertainty relating to slick movement, precise predictions of overall fate are still difficult to achieve.

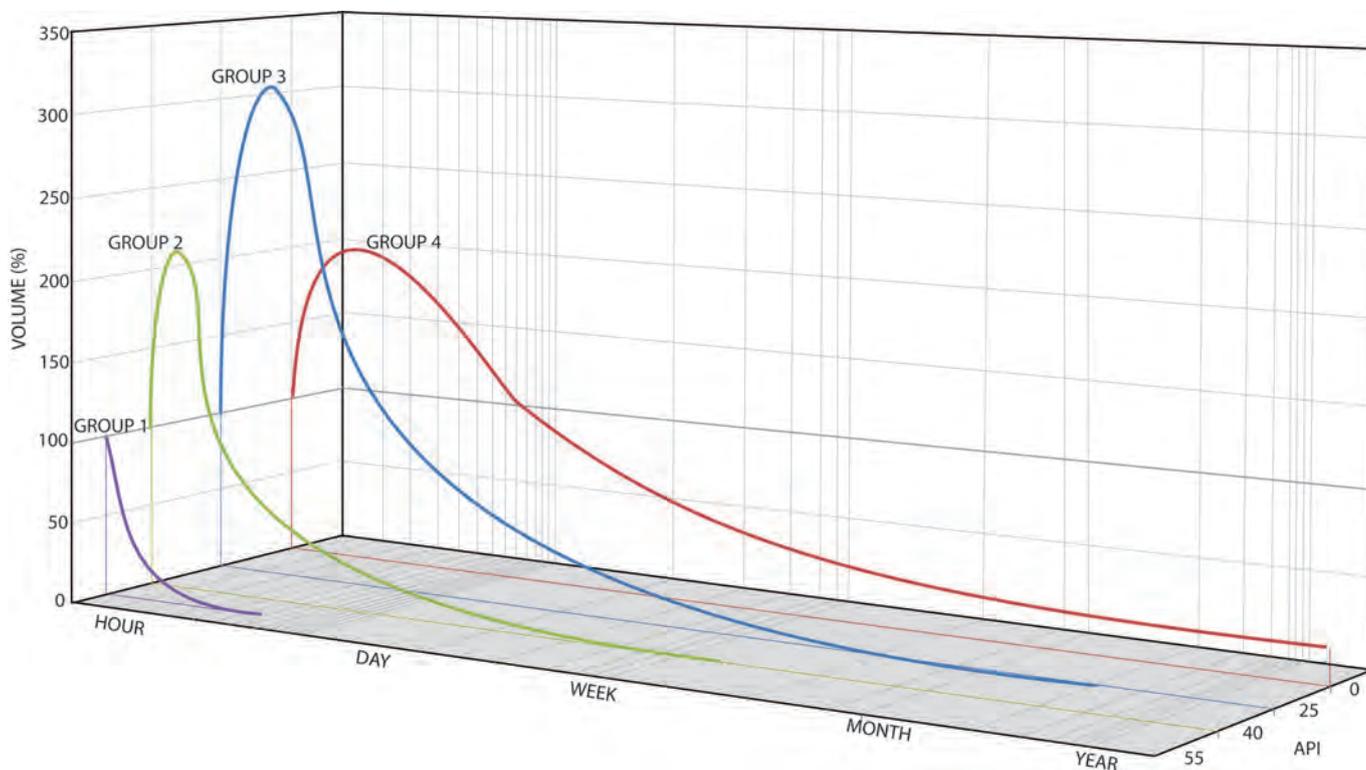
It is therefore important to understand the assumptions upon which weathering and trajectory models are based and to take these into account when using the results. In response operations, for example, model predictions should be verified by observations of actual oil distribution and behaviour. On the other hand, such models provide a useful indication of where such surveys should be focused and the probable fate and behavior of a particular oil. They are also valuable in the context of evaluating optimal clean-up techniques, for training and in the contingency planning process.

## Implications for clean-up and contingency planning

The tendency of oil to spread and fragment rapidly, especially in rough sea conditions, will always place constraints on any response technique and should not be underestimated. For instance, ship-borne oil recovery systems, with swath widths of typically only a few metres, will be unable to encounter any significant quantities of oil once it has spread and scattered over several kilometres. In the case of low viscosity oils, this can happen in just a few hours. This is one of the main reasons that oil recovery operations at sea rarely achieve the removal of more than a fraction of a large slick.

The movement of slicks and the changing nature of the oil through weathering can determine whether any response, beyond monitoring the dissipation of the slick, is necessary. Where an active response is called for, the weathering processes will require the suitability of selected clean-up techniques to be re-evaluated and modified as the response progresses and conditions change. For example, dispersants applied at sea reduce in efficiency as the oil spreads and as oil viscosity increases. Depending on the characteristics of the particular oil, many dispersants become significantly less effective as the viscosity approaches 10,000 cSt and most cease to work at all when the viscosity rises much above this value. Oil viscosity can increase very quickly, meaning the time available for using dispersants can be very short. Consequently, dispersant application should be regularly monitored and spraying operations terminated if ineffective (*Figure 14*).

Similarly, if mechanical recovery systems are deployed, the type of skimmers and pumps used may need to be changed as the oil weathers, its viscosity rises and emulsions form. For example, oleophilic (oil attracting) disc skimmers rely on oil adhering to the disc for recovery (*Figure 15*). However, an emulsion acts as a 'shear-thinning' fluid such that when a twisting movement is applied, for example by a spinning disc, the water droplets in the emulsion align all in one direction, reducing viscosity and causing the emulsion to be sliced through rather than adhering to the disc. The same effect occurs with centrifugal pumps, where the pump impellor may spin without efficient movement of the emulsion through the pump. For this reason, positive displacement pumps are recommended for the transfer of emulsions.



▲ *Figure 13: The volume of oil and water-in-oil emulsion remaining on the sea surface shown as a percentage of the original spill volume (100%) for a typical oil from each of the groups shown in Tables 1 and 2. The curves represent an estimated 'average' behaviour for each group. However, the behaviour of a particular crude oil may differ from the general pattern depending on its properties and the environmental conditions at the time of the spill.*



▲ Figure 14: High oil viscosity has resulted in unsuccessful dispersant application, noted by the typical white plume of dispersant around the oil.



▲ Figure 15: Disc skimmer working successfully in a freshly spilled light crude oil. However, were the oil to become significantly emulsified, the effectiveness of the recovery operation would reduce due to the inability of the emulsion to adhere to the discs.

An understanding of the likely fate and behaviour of different oils and the constraints that these impose on clean-up operations is fundamental to preparing effective contingency plans. In addition, information on the prevailing winds and currents throughout the year will indicate the most likely movement of the oil and the sensitive resources that might be affected in a given location. Data on the types of oil handled and transported can enable predictions to be made regarding the probable lifetime of slicks and the quantity and nature of the remaining oil that may require a clean-up response. It will also help to determine the selection of appropriate clean-up techniques and equipment.

For fixed installations such as oil terminals and offshore loading and unloading buoys, where a limited number of oil types are involved and prevailing weather and sea conditions may be well known, fairly accurate predictions can be made. This simplifies the development of an effective contingency plan and permits the appropriate response arrangements to be put in place. In areas of dense ship traffic, with many vessels in transit, or where a wide range of oil types are handled, the plans cannot cover all eventualities. It is therefore even more important that the type and behaviour of the oil spilled is established at the earliest opportunity so that, if a response is required, the most appropriate techniques can be used.

## Key points

- Once spilled, oil begins to weather and its physical and chemical characteristics change over time.
- Spreading, evaporation, dispersion and emulsification are important in the early stages of the spill whereas photo-oxidation, sedimentation and biodegradation are long-term processes that determine the ultimate fate of the oil.
- The speed with which these processes occur depends on weather conditions and characteristics of the oil such as specific gravity, volatility, viscosity and pour point.
- Evaporation and dispersion account for the removal of oil from the sea surface, while emulsification leads to its persistence and an increase in the volume of pollutant.
- Interaction with shorelines can lead to oil removal through the formation of clay–oil flocculates or to its persistence in sheltered locations by incorporation in fine sediments or the formation of asphalt pavements when mixed into coarse shingle or pebble beaches.
- A small number of residual oils are sufficiently dense to sink when spilled. However, most oils will float and may sink only if mixed with denser sediment.
- An understanding of the likely fate and behaviour of an oil allows response options to be optimised.

## TECHNICAL INFORMATION PAPERS

- 1 Aerial Observation of Marine Oil Spills
- 2 Fate of Marine Oil Spills
- 3 Use of Booms in Oil Pollution Response
- 4 Use of Dispersants to Treat Oil Spills
- 5 Use of Skimmers in Oil Pollution Response
- 6 Recognition of Oil on Shorelines
- 7 Clean-up of Oil from Shorelines
- 8 Use of Sorbent Materials in Oil Spill Response
- 9 Disposal of Oil and Debris
- 10 Leadership, Command & Management of Oil Spills
- 11 Effects of Oil Pollution on Fisheries and Mariculture
- 12 Effects of Oil Pollution on Social and Economic Activities
- 13 Effects of Oil Pollution on the Environment
- 14 Sampling and Monitoring of Marine Oil Spills
- 15 Preparation and Submission of Claims from Oil Pollution
- 16 Contingency Planning for Marine Oil Spills
- 17 Response to Marine Chemical Incidents

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