4.2 Oil spills
4.2.1 Composition of petroleum

Oil is a natural product which results from the once-living materials remains fossilized over millions of years, under extreme conditions. Petroleum oil is a dark colored, flammable liquid found throughout the world in underground pockets in the earth’s outer layer of rocks. It is not just one simple organic compound, but is a mixture of hundreds, maybe thousands of chemical compounds.

In general, these chemicals consist mainly of hydrogen and carbon atoms (the so-called hydrocarbons), giving the oil its hydrophobic character, but that may be all that the individual components have in common.

To distinguish between the different components, one can look at the general chemical class they belong to:

- **If the molecules contain only single bonds**, they are named **alkanes**, saturated hydrocarbons or paraffins. Their general formula is $C_nH_{2n+2}$.
  - Lighter paraffins ($C_5H_{12}$ to $C_8H_{18}$) are refined into petrol;
  - the ones from $C_9H_{20}$ to $C_{16}H_{34}$ are used for the production of diesel fuel, kerosene and jet fuel.
  - The ones that are even heavier exist as solids at ambient temperature. Paraffin waxes are alkanes with around 25 carbon atoms.
  - Lighter molecules (methane, ethane, propane and butane) are in a gaseous state at ambient temperatures.

- A second group is that of the **cycloalkanes or naphthenes**. These are saturated hydrocarbons which have one or more carbon rings to which hydrogen atoms are attached according to the formula $C_nH_{2n}$. Cycloalkanes have similar properties to alkanes but have higher boiling points.

- The **aromatic hydrocarbons** are unsaturated hydrocarbons which consist of one or more six-carbon rings (aromatic or benzene rings). Their general formula is $C_nH_n$. Some of these components, such as benzene, toluene, ethylbenzene or xylene (abbreviated the BTEX components) are known carcinogens.

- Asphalt and bitumen are the heavy-weight hydrocarbon mixtures that are solid at ambient temperature. They usually consist of mixtures of large polyaromatic hydrocarbons.

The average composition of mineral oils has been given in Table 4-2.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Average</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>30%</td>
<td>15 to 60%</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>49%</td>
<td>30 to 60%</td>
</tr>
<tr>
<td>Aromatics</td>
<td>15%</td>
<td>3 to 30%</td>
</tr>
<tr>
<td>Asphaltics</td>
<td>6%</td>
<td>remainder</td>
</tr>
</tbody>
</table>

*Table 4-2. Average composition of mineral oil*

Another more practical way to distinguish among the components of a crude oil, uses **how easy the components are dealt with after a spill**.

- **non-persistent oil** (which is a petroleum based oil that consists of hydrocarbon fractions of which at least 50% by volume distils off at 340°C and 95% by volume at 370°C) and
**persistent oil** ("All oils which are not within the category of nonpersistent oil").

This definition is the same as the one used by the Environmental Protection Agency (EPA) in the USA and the USA Coast Guard. The EPA and the Coast Guard define **five basic groups**.

- Group 1 consists of the non-persistent oils (jet fuels and gasoline).

The persistent oils are then classified further on the basis of their **specific gravity**, as follows:

- Group 2 oils have a specific gravity less than 0.85;
- Group 3 oils have a specific gravity between 0.85 and 0.95;
- Group 4 oils have a specific gravity between 0.95 and 1.0;
- Group 5 oils have a specific gravity equal to or greater than 1.0.

The National Oceanic and Atmospheric Administration (NOAA) of the USA uses a slightly different distinction:

- **Type 1**: Very Light Oils (jet fuels and gasoline, the non-persistent oils from above)
- **Type 2**: Light Oils (such as diesel and light crudes)
- **Type 3**: Medium Oils (most crude oils)
- **Type 4**: Heavy Oils (such as Heavy Crude Oils, No. 6 Fuel Oil, or Bunker C)

<table>
<thead>
<tr>
<th>Volatility</th>
<th>Very Light</th>
<th>Light</th>
<th>Medium</th>
<th>Heavy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile after one or two days</td>
<td>very volatile</td>
<td>up to one-third of spill</td>
<td>two thirds remaining after a few days</td>
<td>little or none</td>
</tr>
<tr>
<td>Volatile after a few days</td>
<td>very volatile</td>
<td>up to one-third of spill</td>
<td>two thirds remaining after a few days</td>
<td>little or none</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Toxicity</th>
<th>Very Light</th>
<th>Light</th>
<th>Medium</th>
<th>Heavy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toxicity</td>
<td>none</td>
<td>moderately</td>
<td>severe and long-term</td>
<td>severe and long-term</td>
</tr>
<tr>
<td>Impact on intertidal areas</td>
<td>none</td>
<td>potentially long-term</td>
<td>severe and long-term</td>
<td>severe</td>
</tr>
<tr>
<td>Impact on sea birds and mammals</td>
<td>moderate</td>
<td>moderate</td>
<td>severe</td>
<td>severe</td>
</tr>
<tr>
<td>Clean-up</td>
<td>impossible</td>
<td>can be effective</td>
<td>can be effective</td>
<td>shoreline clean up difficult; long term contaminataion of sediments</td>
</tr>
</tbody>
</table>

**Table 4-3.** Types of oil and their physical properties. After Davis et al. 2004

- The components that belong to the Very Light Oils are rather toxic (as they are reasonably soluble in the water column) as well as highly volatile (they are supposed to evaporate within 1–2 days), which makes clean-up nearly impossible.
- The other types are moderately volatile to non-volatile. Still one third remains of the Light Oils after a few days, and two thirds of the Medium Oils.
- Medium and Heavy Oils can have severe effects on sea birds and sea mammals.
- Light and Medium Oils can be cleaned when one acts swiftly and effectively; Heavy Oils are difficult to clean up and are bound to contaminate the sediments on the location of the oil spill severely. More details are given in Table 4-3.
4.2.2 Sources of oil contamination
Crude oil has been a part of the natural marine environment for millennia; oil seeps add an estimated $90 \times 10^6$ gal/year. Today, total input of oil into the sea is perhaps ten times greater, with most of the additional oil coming from human’s activities. The public generally takes notice of the problem of marine oil pollution when an oil tanker breaks up in seas or a disaster occurs, one example being the Deepwater Horizon incident in the Gulf of Mexico in spring 2010. In such cases, 205 million gallons were lost during the accident at that oil platform. During the Gulf War in 1991, around 9 million barrels of oil were lost when Iraq set fire to the oil wells. In either case oil slicks often drift towards the coasts and kill seabirds and marine mammals such as seals.

- Yet in reality, oil tanker disasters account for only around 10% of global marine oil pollution.
- Most of the oil enters the seas along less obvious pathways, making it correspondingly difficult to precisely estimate global oil inputs into the marine environment.
- Around 5% comes from natural sources, and
- approximately 35% comes from tanker traffic and other shipping operations, including illegal discharges and tank cleaning.
- Oil inputs also include volatile oil constituents which are emitted into the atmosphere during various types of burning processes and then enter the water. This atmospheric share, together with inputs from municipal and industrial effluents and from oil rigs, accounts for 45%.
- It is well known that the major part of the oil getting into the marine environment originates from evaporating hydrocarbons in tankers/storage, which may be as much as 3.75 million tonnes/year.
- A further 5% comes from undefined sources.
4.2.3 Fate of spilled oil
During the first few hours or even during the first few weeks, the oil is modified by chemical and physical processes: Even when left alone, spilled oil undergoes a number of physicochemical transformations that will lead to its eventual breakdown (see Figure 4-3 for an overview of the processes and Figure 4-4 for how they follow each other during the time after a spill).

**Spreading out:** First of all, an oil spill will spread out (expand) over a large part of the sea surface. This is a physical diffusion process which depends on the viscosity of the oil (and therefore indirectly on the temperature of the surroundings) and which is accelerated by wind and waves.

**Drifting:** In addition, an oil spill can start to drift on the ocean, mainly driven by the waves, in one general direction.

*Figure 4-3. Natural degradation of an oil spill*

**Evaporation:** The lighter components of the oil will evaporate within a few days (and the more a spill spreads out, the more it will evaporate). The amount that evaporates can be quite substantial. For example, of all the oil that ended up in the sea due to the accident with the Amoco Cadiz (1978, 223,000 tonnes of oil lost—Figure 4-5), 40% was evaporated within three days.

**Photo-oxidation:** Sunlight is able to promote the reaction of the oil components with oxygen gas in the atmosphere (a process called photo-oxidation). This process breaks the oil down into water-soluble components or components that will beach under the form of tar balls.

**Emulsification:** The part on top of the surface can be mixed by wind and waves to form a red-brown water in oil emulsion (which is often called chocolate mousse due to its texture and aspect). Some are very stable, others break down by heating or action of the sun. The formation of the viscous emulsification (chocolate mousse) can increase the original volume of the oil as much as fourfold, rendering the use of
chemical dispersants impossible and making it far more difficult to pump the oil off the water surface.

**Dispersion:** Another part will **disperse** in the water. Here the oil will first break up in small droplets, which will then sink to deeper water levels.

**Dissolution:** Later on, the molecules in the droplets will even **dissolve** completely in the water (especially the relatively more water soluble, smaller components in the mix, such as benzene and toluene). Many oils also become stickier over time (a process called **weathering**).

**Biodegradation:** The more an oil is dispersed and dissolved in the water column, the faster the organisms (bacteria, fungi, and yeasts) in the water will start with its **biodegradation** to CO₂ and water.

**Sedimentation:** Some heavier oils, with a higher density than seawater, are deposited on the sea bottom or the **sediments** in the shorelines. Other components can **adsorb** to the surface of the material floating in the water column; these materials can sink to the bottom as well.

**Figure 4-4.** Succession in time of the physicochemical processes that transform an oil spill.

Processes such as sedimentation and breakdown by bacteria, may continue for months or even years, although in some cases, under favorable conditions, they may be completed within a matter of days.

**The reason for this discrepancy is that,**

**Firstly,** the various substance groups contained in the oil undergo biological breakdown at different rates. The speed of breakdown depends primarily on the molecular structure of the oil constituents. The more complex the hydrocarbon molecules, the longer it takes for the oil to be broken down by microorganisms.

**Secondly,** the rate at which the various hydrocarbons are broken down is increased by the following factors:

- high temperatures, promoting bacterial activity;
- a large surface area (if necessary, the surface area of the slick can be increased through the use of dispersants, i.e. surface-active agents [surfactants] which promote the formation of dispersions);
- good oxygen supply for the bacteria;
- good nutrient supply for the bacteria;
- low number of predator organisms which would reduce the number of bacteria.
Different types of oil demonstrate a different behavior and reactivity to their physicochemical environment.

- Most crude oil mixtures emulsify into a stable foam.
- Over 70% of a Fuel Oil No. 6 spill will be left over, either floating or beached, for a week or longer.
- In contrast, diesel evaporates or disperses spontaneously for about 90% within a few days or even hours.

When it comes down to specific components:

- toluene, xylene, propane, ethylacrylate, methanol, acetone and ammonia evaporate
- ammonia, ethylacrylate, hexanol, sulfuric acid, methanol and acetone dissolve
- hexanol, toluene, dioctylphthalate and xylene tend to float
- creosote and trichloroethylene sink to the bottom.

**Figure 4-5.** Famous oil spills. Above Left: Amoco Cadiz (Source: NOAA), Above Right: Exxon Valdez (Source: NOAA), bottom: Deepwater Horizon (Source: US Coast Guard)

### 4.2.4 Effects of oil on sea life

Oil spills, and how animals are confronted with these spills, have become the typical image of marine pollution (**Figure 4-6**).

- The first effect of oil pollution on animals is purely **physical**.
  - Firstly, the oil blocks the diffusion of atmospheric oxygen into the water, impeding the respiration of all water creatures.
  - Additionally, oil **sticks easily** to the skin, fur or feathers of marine animals, disrupts their normal structure and obliterates their ability to trap oxygen bubbles between the hairs or feathers, which leads to a loss of their insulating properties.
  - Their buoyancy, and therefore also the ability of the animals to swim is affected.
The more the oil sticks (especially crude fuels and bunker fuels), the more the animals are subjected to hypothermia and stress. Furthermore, when the animals try to clean themselves, and groom their fur to get rid of the sticky oil layer, they are bound to ingest a part of it. Also, some fish are attracted to oil because it looks like floating food. Thicker sludge can cover the gills of the fish in the neighborhood of a spill; volatile components are inhaled and enter the bloodstream through the lungs of birds and mammals.

![Figure 4-6. Victims of the Exxon Valdez oil spill.](image)

The oil that has been internalized, one way or another, can exert toxic effects on the animals: the oil attacks the mucosa of the gastrointestinal system, leads to ulcers, diarrhea and, if worse comes to worst, internal bleeding and organ damage. The oil also changes the sensitivity of the animal for parasites. The animals will suffer from anemia and immunotoxic effects, and have a diminished reproductive success.

**Age- and species specific effects**

- The oil spill can have age- and species specific effects as well. For example, fur seal pups are affected more than adults by oil spills because pups swim in tidal pools and along rocky coasts, whereas the adults swim in open water where it is less likely for oil to linger.
- Dugongs feed on sea grass along the coast and therefore be more affected by oil spills.
- In whales, the baleen plates will be clogged, and the nesting habitat of marine turtles can be destroyed.

All in all, the effect of an oil spill on the local fauna can be disastrous. Moreover, a number of possible consequences (such as the incidence of carcinogenesis or other long-term effects) has not been studied in great detail.
4.2.5 How is oil pollution cleaned up?

To combat an oil spill (which means, to first block its movements so that it won’t overrun the shore with touristic activities or valuable ecosystems, and to remove the oil later on) several methods can be used, depending on the type of oil, the quantity, the location and the local weather conditions.

Firstly, a cleaning party will try to contain the spill with oil booms (Figure 47). Booms are gigantic pieces of plastic, that will block further spreading and drifting by acting as a fence. Booms can consist of mere plastic cylinders, with added weights at the bottom, so that they float closely to the surface.

Sorbent booms will consist of a material capable of absorbing the oil.

A third type are the fire booms. They are made out of metal, so that they are able to contain oil spills until they can be set on fire. Specialists are against this last method, as this will turn the oil spill in the water into a huge cloud of toxicants, which will often fall out over land, on crops and inhabited areas… (see https://www.youtube.com/watch?v=chW9T7OADWk)

Secondly, they will adsorb the oil to sawdust, straw, foam chips, … or the sorbent booms mentioned in the previous paragraph. Sorbents are often used to finish the cleaning operation, and meant to remove the last traces of oil which could not be skimmed off. The sorbents are added manually and recovered with nets or rakes. This method is useful for smaller spills and near the coastlines, but not for larger ones and in open sea.

Thirdly, they will use boats that can skim the oil from the water surface (short: skimmers). These boats pump the oil in the settling tanks they carry. In there, the oil and water can separate out. The oil layer can be refined again (if it is still fresh enough), or be burned.

Alternatively, they can use chemicals to disperse the oil in the water column (Figure 4-7). The oil can eventually break down naturally, and chemical dispersants act to speed up the natural process.

On the other hand, if the oil is too close to shallow, coastal waters or other biologically sensitive areas, using the chemicals would only heighten the danger for the local fauna and flora. A classic case of trying to choose between two evils. Clean-up efforts will then choose to forego the dispersants and opt for a more laborious, but more nature-friendly way of removing the spill. Once dispersed, the substance will then drift out into the ocean where micro-organisms will deal with it.

Three groups of bacteria are able to break down spilled hydrocarbons:

– the anaerobic sulfate-reducing bacteria (SRB)
– the anaerobic acid-producing bacteria,
– the general aerobic bacteria (GAB).

These naturally occurring organisms will both degrade the oil components as well as take the place of these bacterial populations that were killed off by the oil, thereby restoring the food chain.

Since the Exxon Valdez, genetically enhanced microbes can be used to favor biodegradation.
**Burning** is a method that is sometimes used to remove oil from the surface of the water, for example in the case of the Deepwater Horizon drilling platform. Oil may also be burned after skimmers remove the oil from the water surface. Nevertheless, this is a method which again **causes more problems than it is worth**.

- The burning of oil releases nitrogen and sulfur, which in turn causes acid rain.
- While burning can remove the oil from the water surface quickly and efficiently, it causes additional pollution.

Moreover, in order to light the fire, one needs the more volatile components in the oil… which evaporate quickly and will probably be missing by the time anyone tries to burn the oil.

Any oil that escapes the cleaning operation and the natural degradation will end up on the nearby shores.

**Manual labour is then the best** and often only solution to prevent most damage (Figure 4-7), and to clean the land along the shores to avoid further ecological disasters. What can be done and should be done depends upon the ecosystems that will suffer from the spill. When all that is over and done, all that remains is hope that the ecosystems in the affected area are resilient enough to undo the damage caused by the spill, and that the organisms are able to deal with the remaining (and often invisible) pollutants.

Table 4-6 gives an overview of the different shoreline types and how vulnerable they are for oil pollution.
<table>
<thead>
<tr>
<th>Vulnerability Index</th>
<th>Shoreline type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Exposed rocky headland</td>
<td>Wave reflection keeps most of the oil offshore. No clean-up necessary.</td>
</tr>
<tr>
<td>2</td>
<td>Eroding wave-cut platform</td>
<td>Wave swept shoreline. Natural processes remove most of the oil within a few weeks.</td>
</tr>
<tr>
<td>3</td>
<td>Fine-grained sand beach</td>
<td>Oil may sink and/or be buried rapidly, making clean-up difficult. Under moderate-to-high energy conditions, oil may persist for several months.</td>
</tr>
<tr>
<td>4</td>
<td>Coarse-grained sand beach</td>
<td>Oil may sink and/or be buried rapidly, making clean-up difficult. Under moderate-to-high energy conditions, oil will be removed naturally within a few months from most of the beach face.</td>
</tr>
<tr>
<td>5</td>
<td>Exposed, compacted tidal flat</td>
<td>Most of the oil will not adhere to, or penetrate into, the compacted tidal flat. Clean-up is usually unnecessary.</td>
</tr>
<tr>
<td>6</td>
<td>Mixed sand and gravel beach</td>
<td>Oil may undergo rapid penetration and burial. Under moderate-to-low energy conditions, oil may persist for years.</td>
</tr>
<tr>
<td>7</td>
<td>Gravel beach</td>
<td>Same as above. Clean-up should concentrate on the high-tide swash area. A solid asphalt pavement may form under conditions of heavy oil accumulation.</td>
</tr>
<tr>
<td>8</td>
<td>Sheltered rocky coast</td>
<td>Areas of reduced wave action. Oil may persist for many years. Clean-up is not recommended unless oil concentration is very heavy.</td>
</tr>
<tr>
<td>9</td>
<td>Sheltered tidal flat</td>
<td>Areas of great biologic activity and low wave energy. Oil may persist for years. Clean-up is not recommended unless oil accumulation is very heavy. These areas should receive priority protection by using booms or oil-sorbert materials.</td>
</tr>
<tr>
<td>10</td>
<td>Salt marsh and mangrove forest</td>
<td>The most productive of aquatic environments. Oil may persist for years. Cleaning of salt marshes, by burning or cutting, should be undertaken only if heavily oiled. Mangroves should not be altered. Protection of these environments by booms or oil-sorbert materials should receive first priority.</td>
</tr>
</tbody>
</table>

Table 4-6. Classification of shorelines in order of increasing vulnerability to oil spills damage.  
(After Gundlach & Hayes, 1978)