Properties and fate of spilled oil

Module 2

Objectives

Develop basic knowledge of the composition of oil (and fracking fluids); how materials change over time; soil strata influence on oil penetration.

Topics

- Properties of crude oil and its derivatives
- Oil and its behavior in the Environment (weathering)
- Contaminated Soil Demonstration
- Factors that affect oil weathering above and below ground

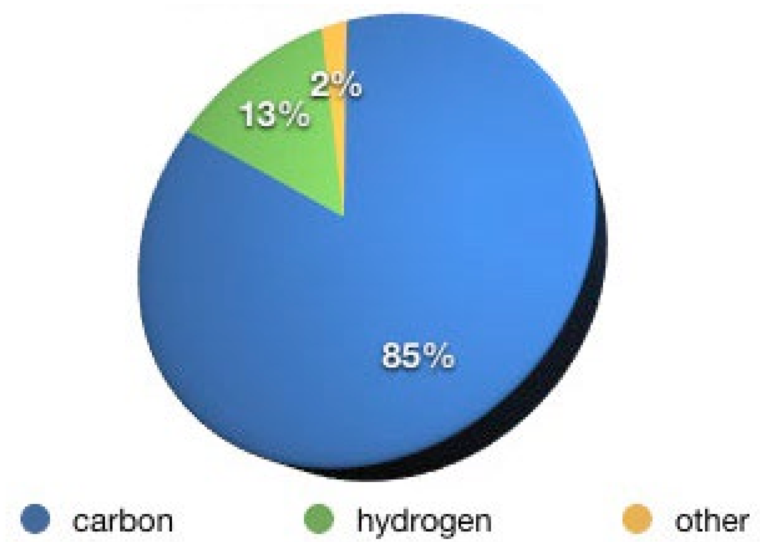
Composition and Properties of Crude Oil

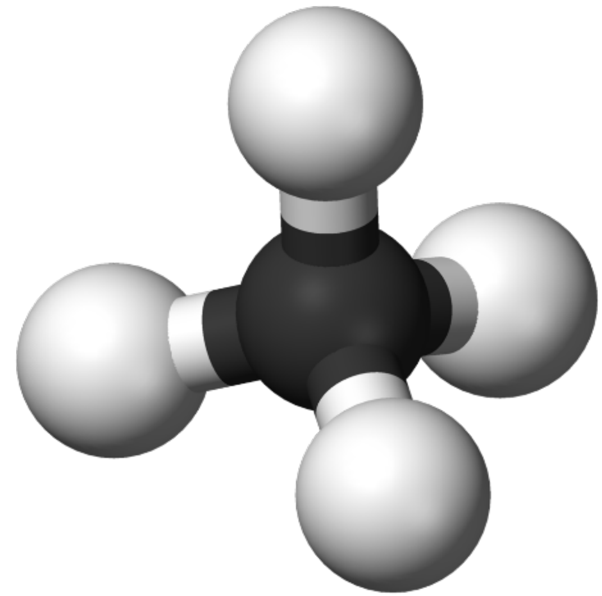
Crude oil (or petroleum) is a liquid comprised of **hydrocarbons**, which are organic compounds that contain small amounts of metals and other elements. The chemical composition of crude oil:

Carbon - 83 to 85%
Hydrogen - 10 to 14%
Nitrogen - 0.1 to 2%
Oxygen - 0.05 to 1.5%
Sulfur - 0.05 to 6.0%
Metals < 0.1%

Crude oil is mostly hydrogen and carbon, but composition varies greatly and depends on origin.

Crude Oil and Methane: two extremes





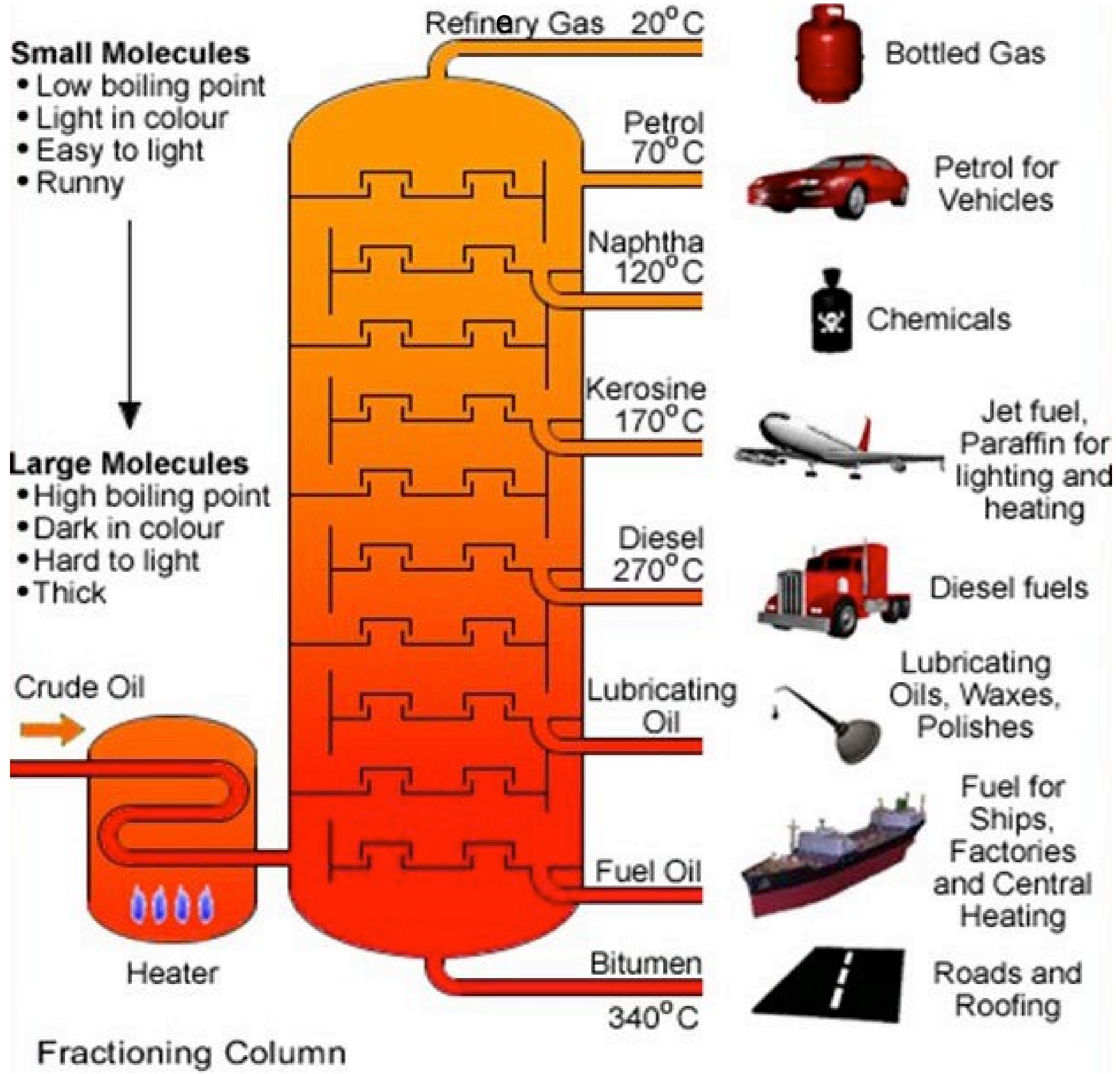
Crude oil formula **CnH2n+2** (where n = positive integer)

"Other" includes small quantities of Oxygen, Sulphur, Nitrogen, Vanadium Nickel and Chromium.

Ball-and-stick model of the **methane** molecule, **CH4**. Methane is the simplest hydrocarbon, part of a group of HCs with similar properties, known as the **alkanes**, which contain single bonds only.

Fractional Distillation of Crude Oil

In an oil refinery



Source: © 2009 science-resources.co.uk

Appearance of Crude Oil

The **colour** of raw crude is usually **dark brown/black** although some fields deliver a **greenish** or sometimes **yellow** crude. Depends on the source and the way the crude was formed.

The **viscosity** also differs. At one extreme, crude can be almost **solid** and requires a significant investment to refine into a useable state as anything other than bitumen. At the other extreme, crude can be a **clear fluid** resembling kerosene, needing minimal refining to be used as fuel.

Note: global reserves of **light crude are almost gone,** so refineries must refine more heavy crudes, at higher cost.

Oil in the Atmosphere: burnt Oil & Emissions

Crude

Diesel ($C_{12}H_{23}$)

Methane (CH_4)

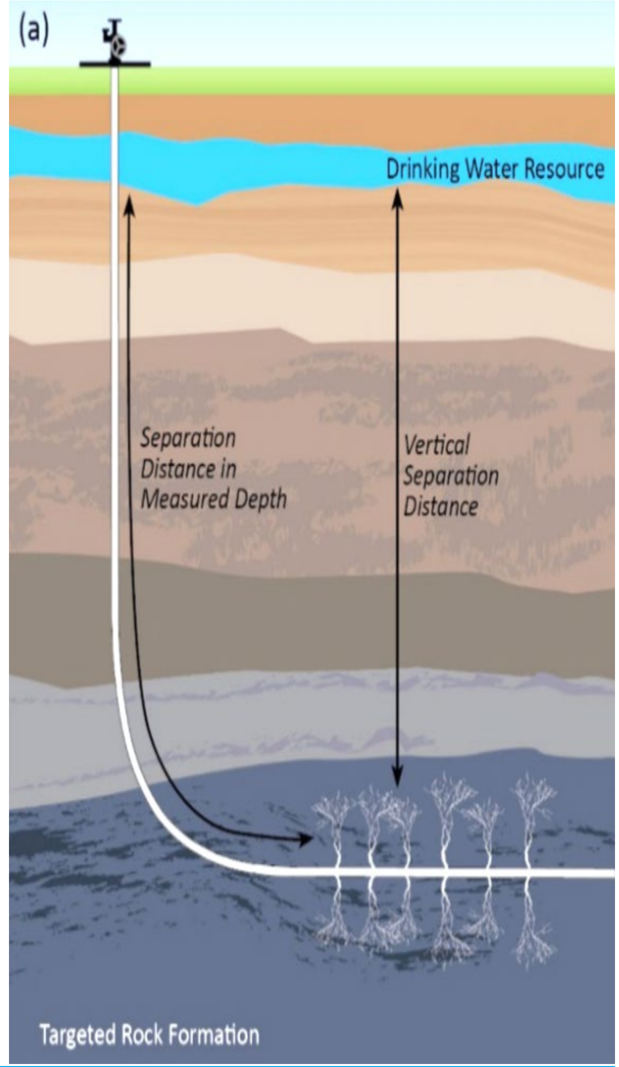
Notice the amount of particulate materials (PMs) in crude and diesel smoke. Temperature combustion of fuels above about 1300°C oxidise some of the nitrogen to NOx gases.

Fracking Fluid Additives and Spill Problems

Of > 1,000 different additives, some are known to be hazardous to human health. Specific compounds used depends on company preference, source water quality and site-specific characteristics of the target formation.

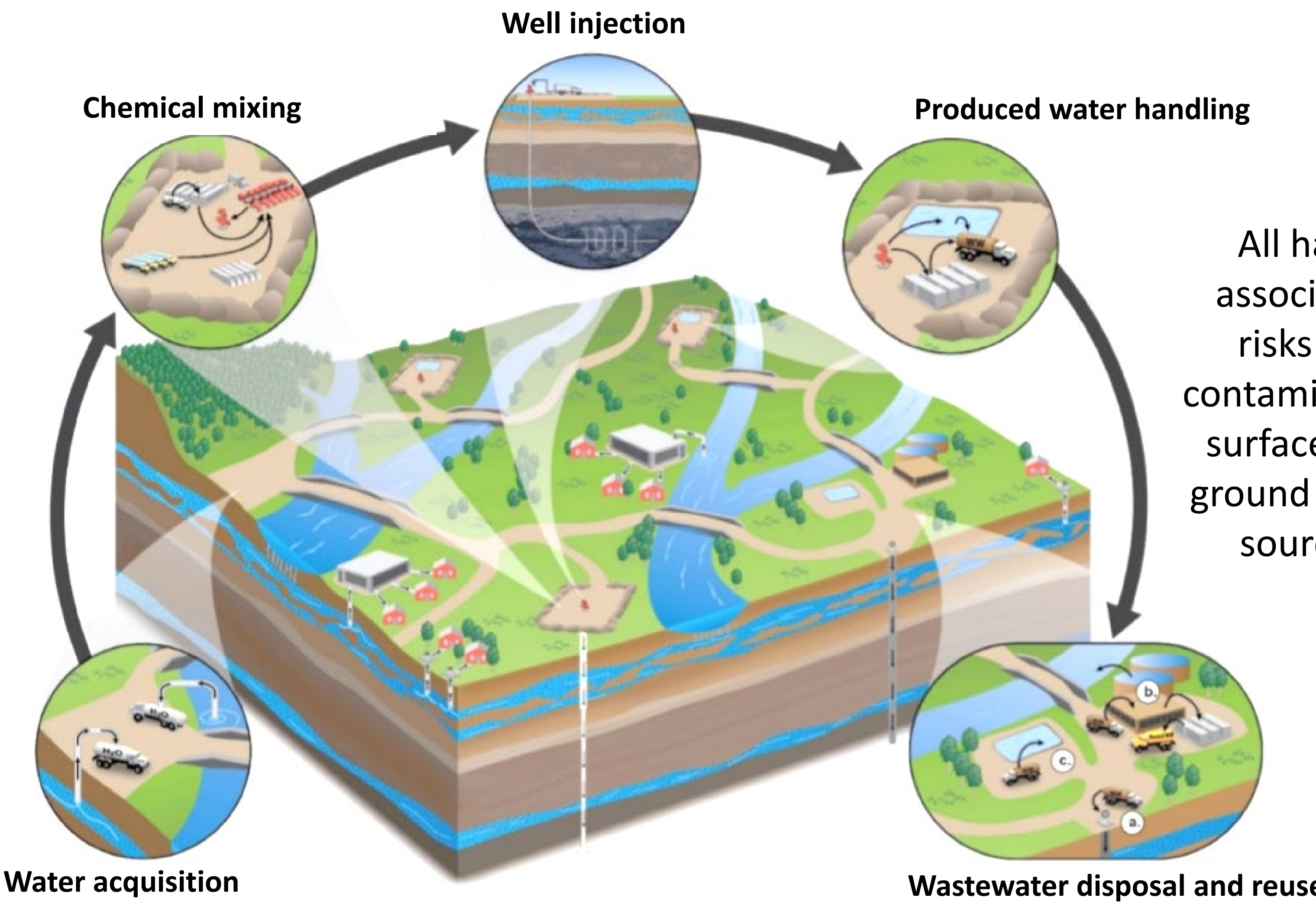
Chronic oral reference values (RfVs) from sources considered by the US EPA were available for ONLY 98 (9%) of 1,084 chemicals used in fracturing.

Approx. 275,000 wells drilled are likely to have been hydraulically fractured between 2000 and 2013. Every year, spills of hydraulic fracturing fluids and additives during the chemical mixing stage of hydraulic fracturing water cycle have reached surface water and groundwater resources. **An ongoing pollution threat.**



Source: U.S. EPA. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States (Final Report). U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-16/236F, 2016.

The five stages of the hydraulic fracturing water cycle



All have associated risks for contaminating surface and ground water sources

Source: U.S. EPA. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States (Final Report). U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-16/236F, 2016.

Oil in the Environment and its Behaviour

Spills range widely in oil type, spill size, location, and environmental conditions during the release.

Type of oil: Heavy, Medium, Light

Oil properties: density, viscosity, flash point, and adhesion; aliphatic vs aromatic; +/- carbon molecules

Climatic conditions:

Temperature

Wind

Oil Spill

Long-term processes: Photo-degradation, Microbial degradation, Auto-oxidation, Sedimentation

Primary processes (days/weeks): Spreading (gravity), Evaporation, Dispersion, Dissolution, Emulsification

Weathering

Frequent end product = Tarsheets or tarballs

Some facts about Spilled Oil

1. The chemical **composition of oil changes** due to weathering.

2. Some oils **weather rapidly** and undergo extensive changes in character, whereas **others remain relatively unchanged** over long periods of time.

3. The effects of **weathering are generally rapid** (1 to 2 days) for hydrocarbons with lower molecular weights as a result of evaporation.

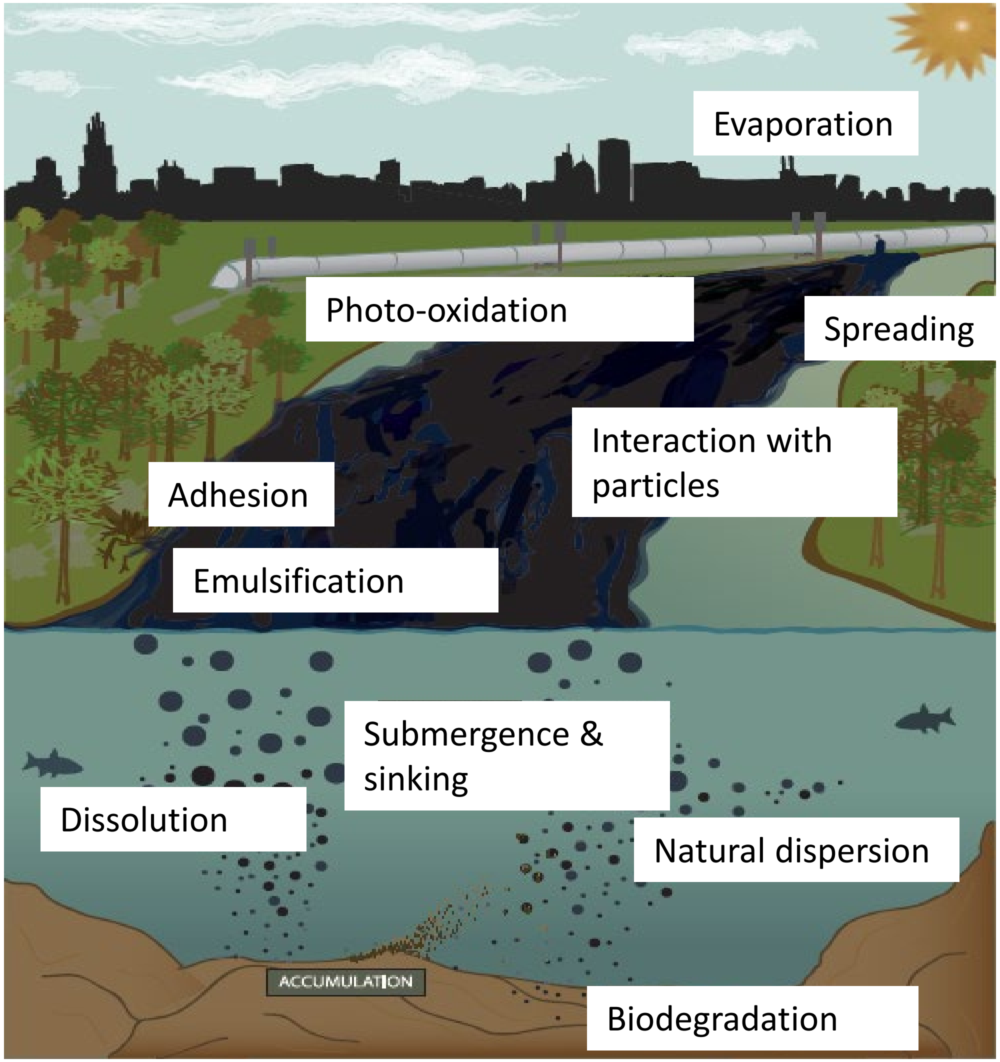
4. **Degradation of the higher weight fractions is slower** and occurs primarily through microbial degradation and chemical oxidation.

5. It is important to recognize the **dynamic nature of spilled oil** and the fact that the properties of spilled oil can change over time.

6. During a response operation, it is crucial to **monitor continuous changes** in properties of spilled oil, as response strategies may have to change.

Source: "4 Behavior and Fate of Oil." Transportation Research Board and National Research Council. 2003. *Oil in the Sea III: Inputs, Fates, and Effects*. Washington, DC: The National Academies Press. doi: 10.17226/10388.

Oil Spill in Rivers (and Sea)



Also affected by:

- Air/water temperature
- Types/amounts of nutrients/ inorganic substances present
- Amounts of suspended sediment
- Geology of riverbanks/shoreline
- Condition of the receiving water body
- Type of oil

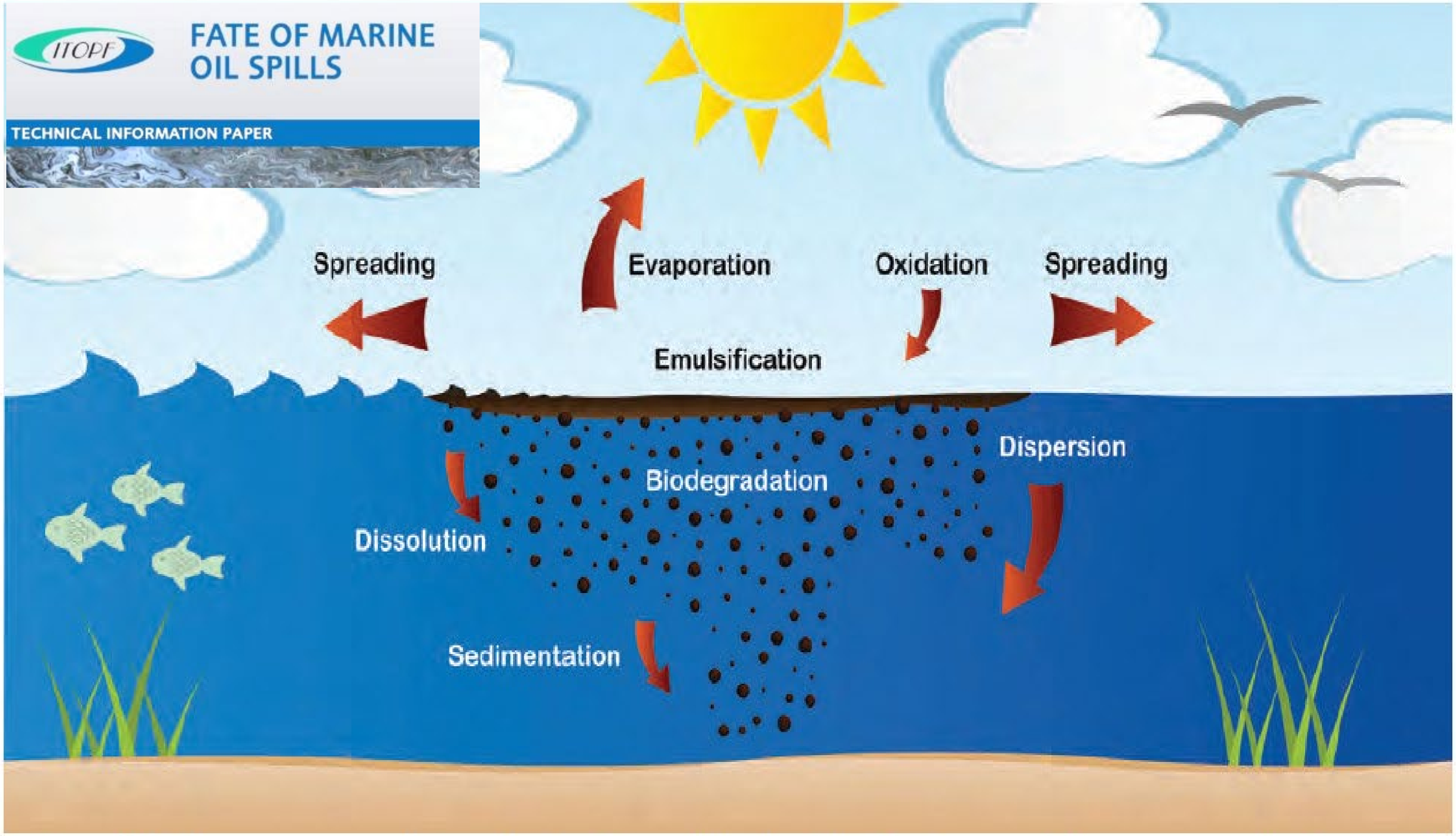
Source: http://local.esso.com/Chad-English/PA/Files/Sect04.prn.pdf

Oil Spill in River in Colombia

In March 2018, oil from the Lizama 158 well, operated by the state-owned company Ecopetrol, spilled and entered into the Lizama and Sogamoso rivers, and has reached the Magdalena river.

Source: https://www.smithsonianmag.com/smart-news/oil-spill-colombia-has-killed-2400-animals-180968653/

Weathering of oil in aquatic environments

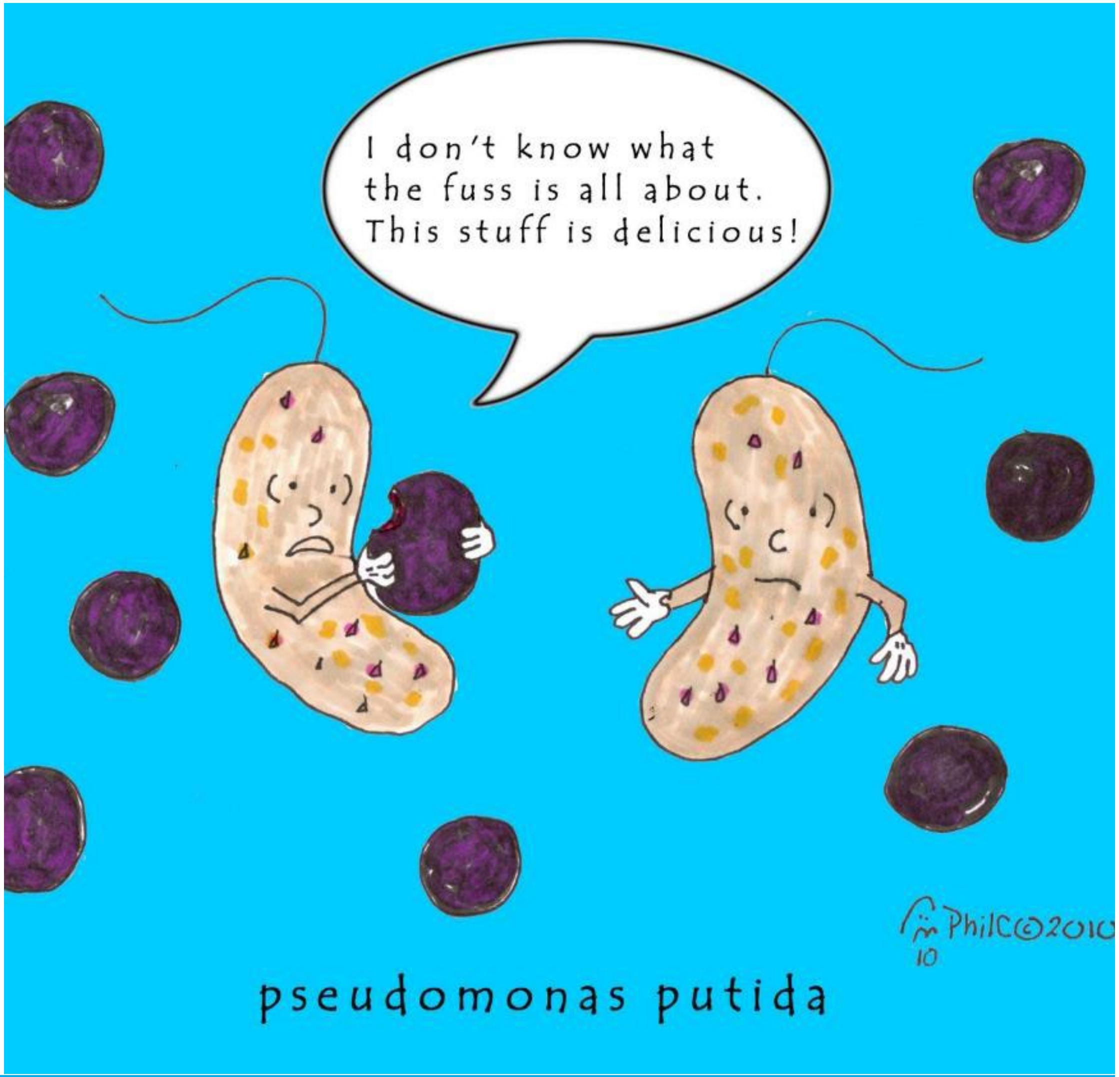


▲ *Figure 4: Weathering processes acting on oil at sea. Once oil strands on the shoreline some of these processes will no longer apply.*

Degradation of oil in aquatic environments

Factors affecting crude degradation in water:

- Water temperature
- Types/amounts of nutrients (e.g. N, P added to a spill will boost microbial action)
- Oxygen availability, as microorganisms need oxygen for their enzyme to function
- Type of oil



Source:

Fate of oil spill on water - depends on oil

Light Distillates (e.g. diesel, jet fuel, kerosene): Low viscosity, spread rapidly into thin sheens, rarely emulsify; evaporate slowly and incompletely (40-50%); moderately persistent; have greatest risk of impacting water-column; readily degraded by aerobic microbial action; short-term persistence in sediments.

Heavy Distillates (e.g. bunker C): High density, lose only <10 % via evaporation; low natural dispersion - too viscous to break into droplets; lowest water-soluble fraction - minimum loadings to water column; quickly break up into thick streamers -> fields of tarballs; highly persistent, for great distances, eventually stranding, posing significant impacts to birds, turtles, etc.; likely to sink after binding with sediment (e.g. sand in surf zone/after stranding).

Crude Oils: Wide range of compounds - light to heavy. About 30% evaporation of 'medium' crude slick in 24 h, but always significant residue. Many emulsify readily -> greatly reduces subsequent weathering rates, spills close to shore often strand/persist on shorelines; tend to adsorb heavily onto intertidal sediments, with risk of subsequent erosion of oiled sediments and deposition in nearshore habitats. Spills offshore -> eventually break into fields of **tarballs** > transported long distances; stranded oil can persist for weeks to years.

Oil on Water

Oil Spill

Type of Oil:
Heavy
Medium
Light

Climatic conditions:
Temperature
Wind/waves
Currents

Suspended sediments
Nutrients (affecting bacterial activity)

Primary processes (days/weeks): Spreading Evaporation, Dispersion, Dissolution, Emulsification

Weathering

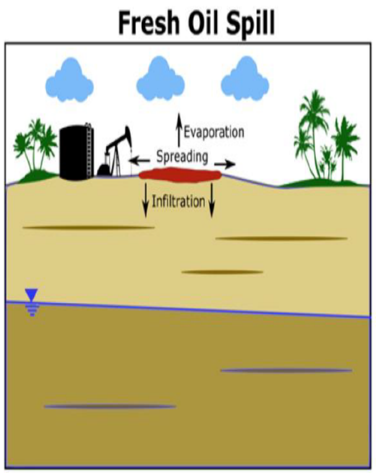
Crude Oil Spill

Oil on land e.g. from artisanal oil refining

Processes affecting fresh oil spills

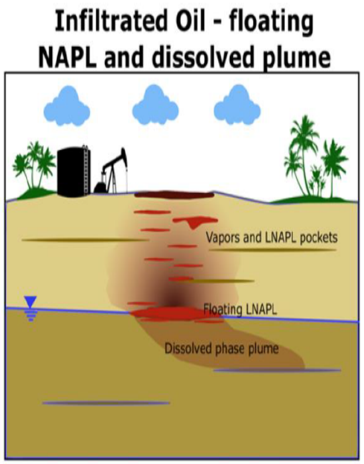
- Evaporation of volatile light HCs
- Spreading, depending on viscosity and topography gradient
- Infiltration, depending on viscosity and soil texture

Time scale days to weeks



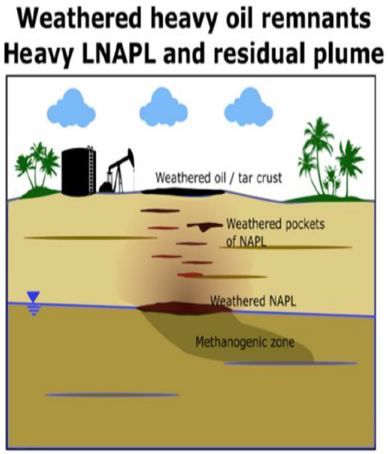
- Formation of NAPL layer
- Sorption of oil to soil matrix
- Volatilisation of light HCs from NAPL
- Dissolution of soluble HCs and formation of dissolved phase plume
- Biodegradation of dissolved phase and vapours

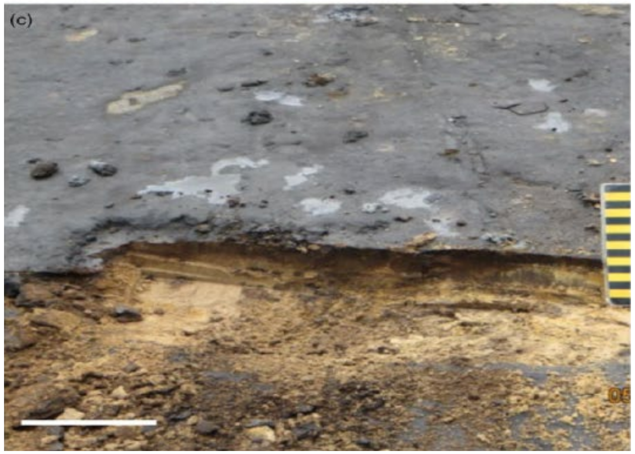
Time scale weeks to months



- Surface oil hardens
- Very limited volatilisation
- Biodegradation induces methanogenic conditions in groundwater
- Enrichment of NAPL with heavy HCs

Time scale years to decades





Oil on Land

Type of Oil:
Heavy
Medium
Light

Climatic conditions:
Temperature
Wind

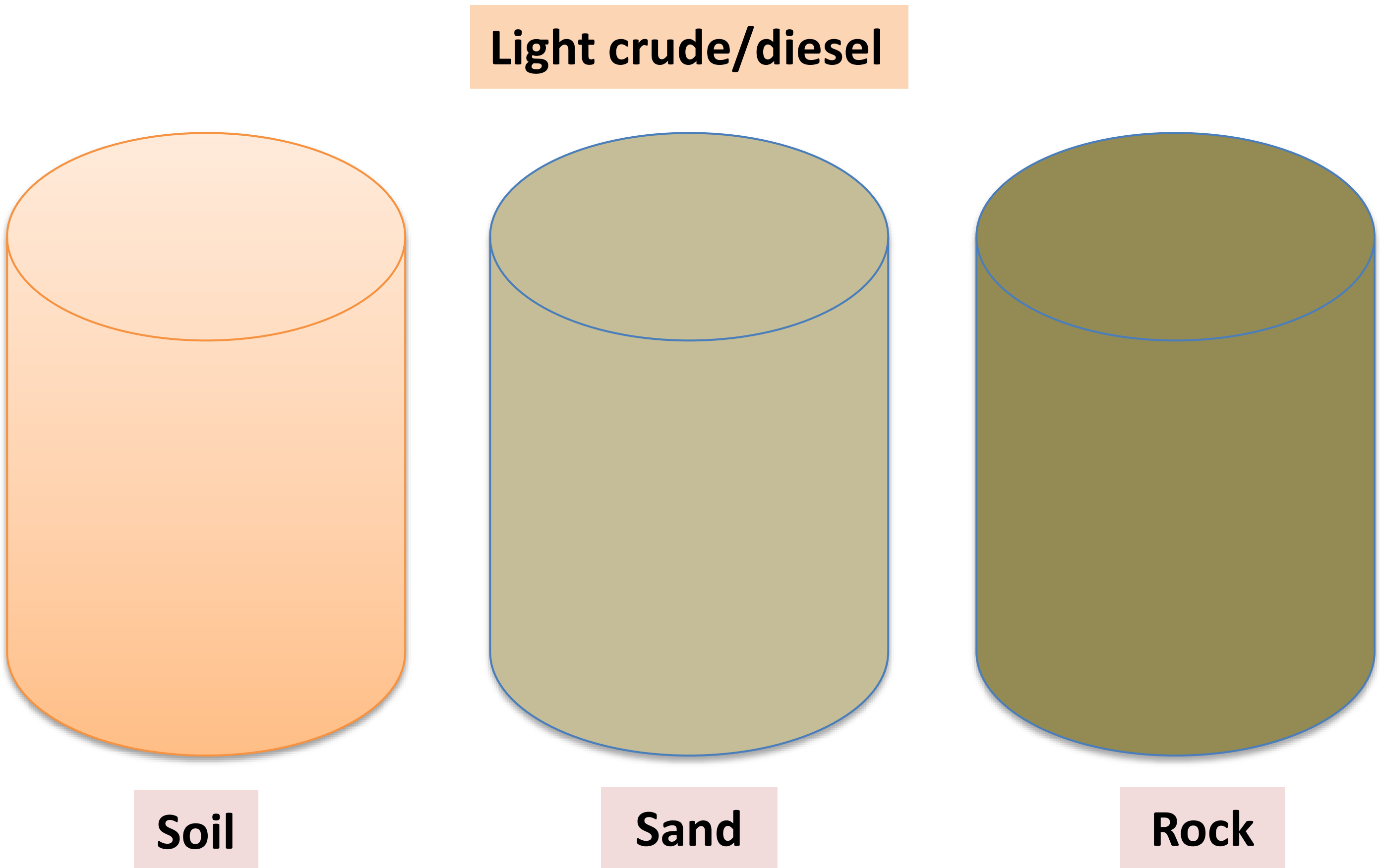
Oil Spill

Soil characteristics:
Grain size
Porosity
Structure-fractures
Water content
Organic matter

Evaporation
Nutrients
(affecting bacterial activity)

Weathering

Contaminated soil **demonstration**



Oil in Soil – Crude oil experiment

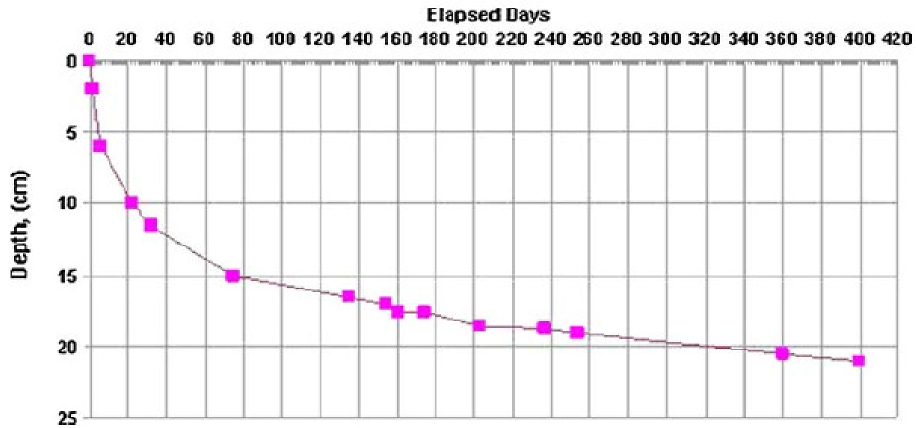


Fig. 2 Infiltration depth versus time for dry sand system

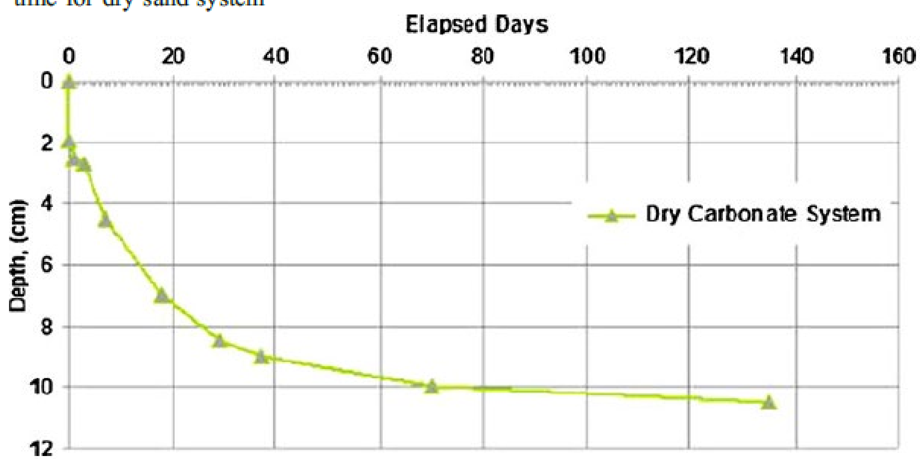


Fig. 3 Infiltration depth versus time for dry carbonate system

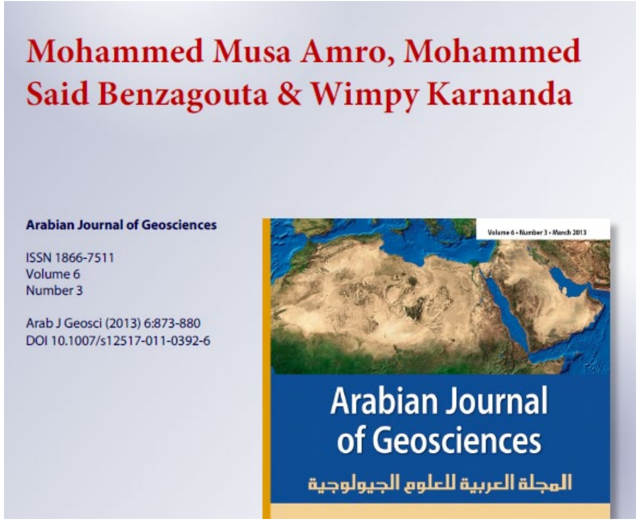
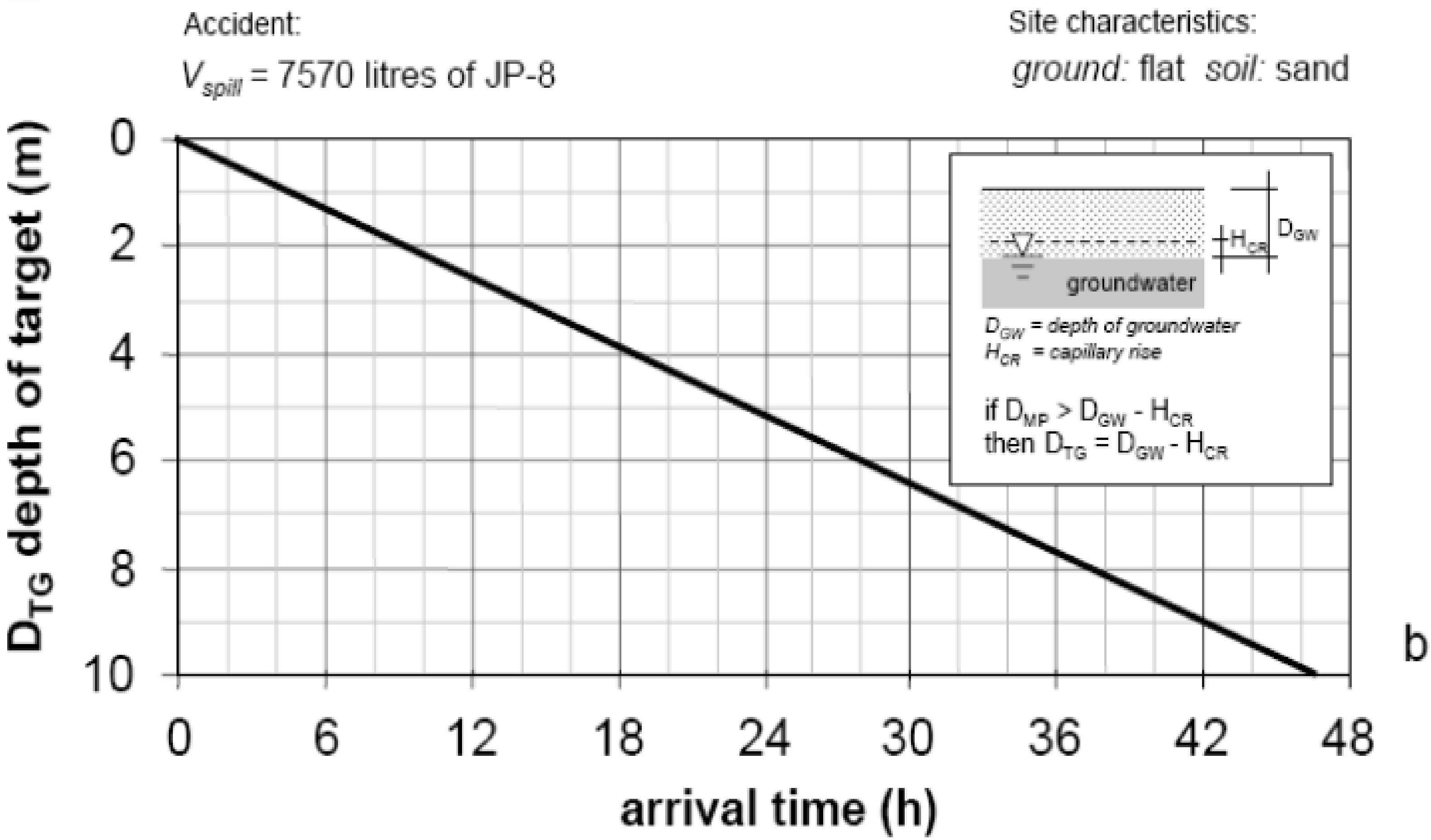


Fig. 1 Depth performance in dry sand (*left*) and dry carbonate (*right*) system

Oil Penetration in Soil – Canada Jet fuel



Oil in Soil Penetration – Romania Crude

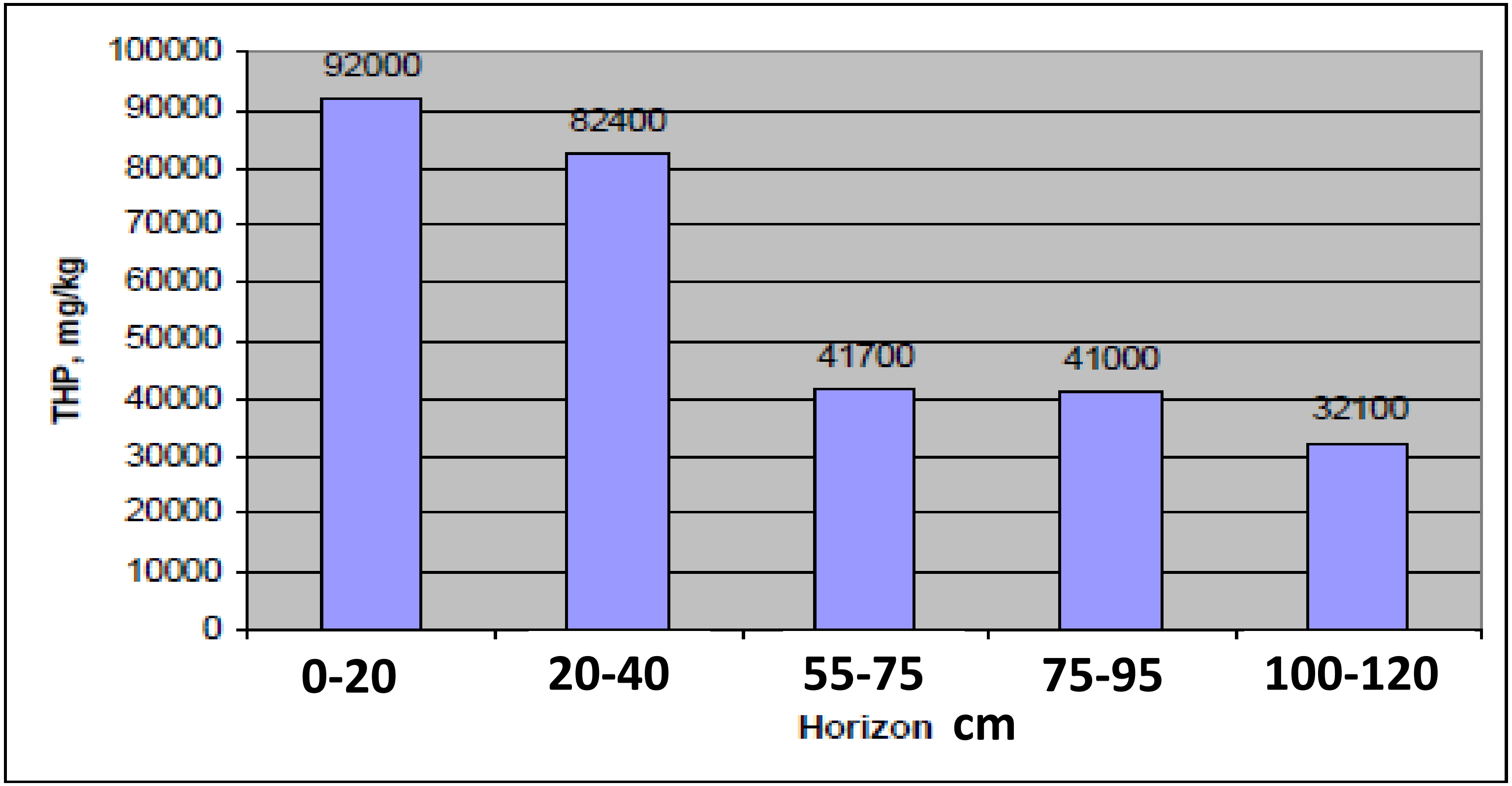


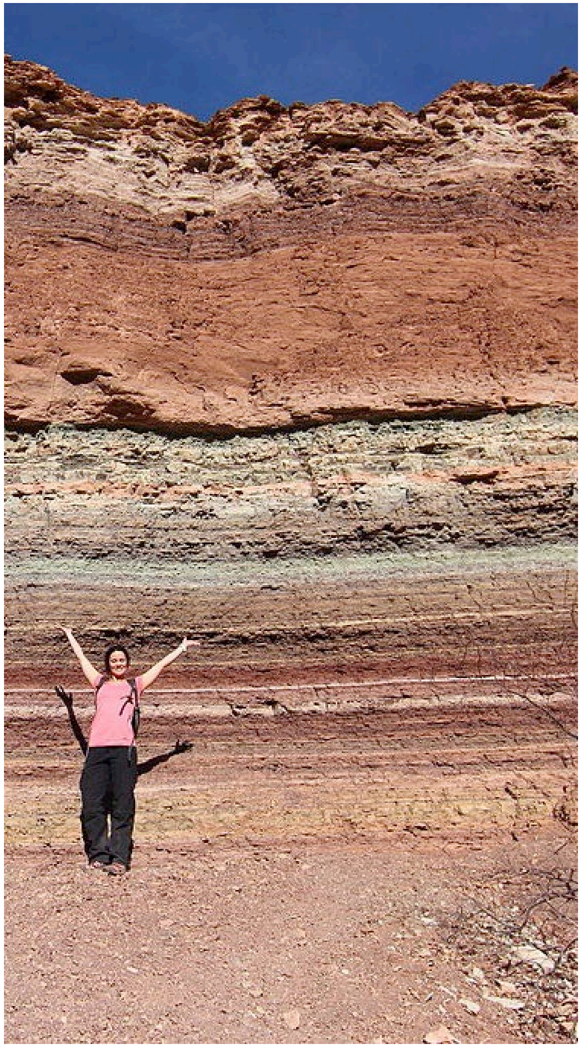
Figure 8 Evolution of total petroleum hydrocarbons in the polluted profile achieved in Perisoru, Braila County

Source: Marinescu et al 2010. An assessment of the effects of crude oil pollution on soil properties. AFST 11(1): 94-99

Soil strata and oil penetration

Stratigraphic features affecting oil penetration:

- Slope of strata, influencing spreading
- Types of strata, and their permeability, with dense rock preventing further vertical penetration and influence lateral spreading
- Presence of faults, causing unpredictable penetration and spreading
- Presence of depressions

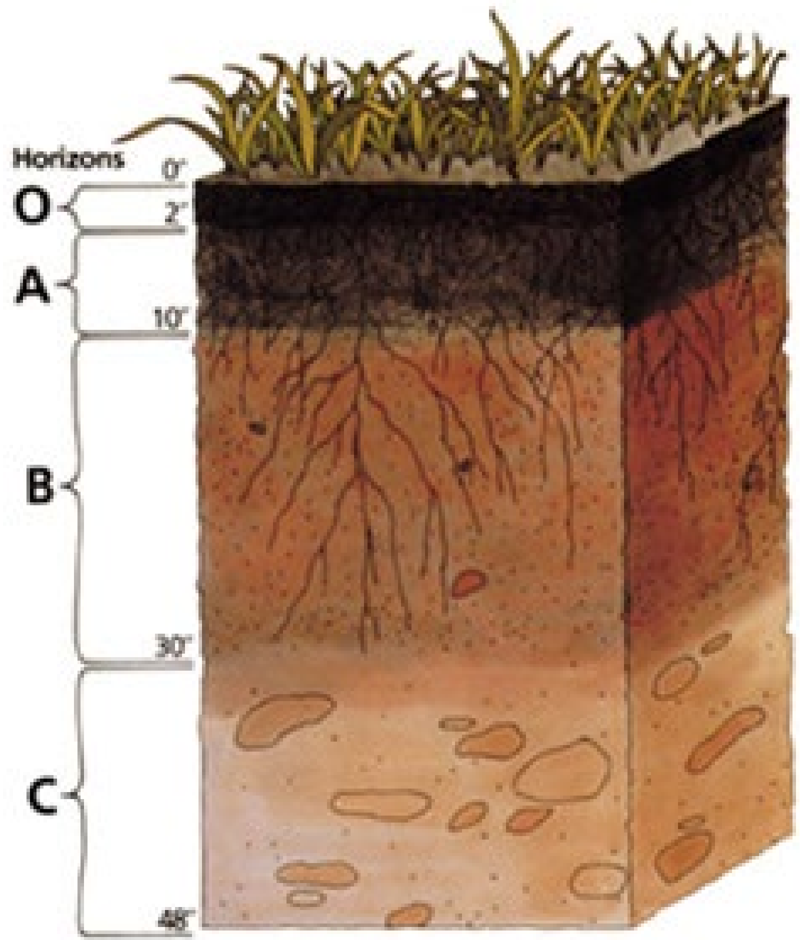


Source:https://fr.wikipedia.org/wiki/Strate_(g%C3%A9ologie)

Soil strata and oil penetration

Grassland soil profile. This soil profile has a surface horizon that has high levels of organic matter. It may be representative of a fertile grassland soil.

Oil penetration of heavier fractions usually restricted to the top 20 cm, with the more soluble and volatile fractions penetrating deeper.



Source: http://soils.usda.gov/education/resources/k_12/l

Oil on Soil - Overview

Evaporation – depends on temperature, weather and oil type

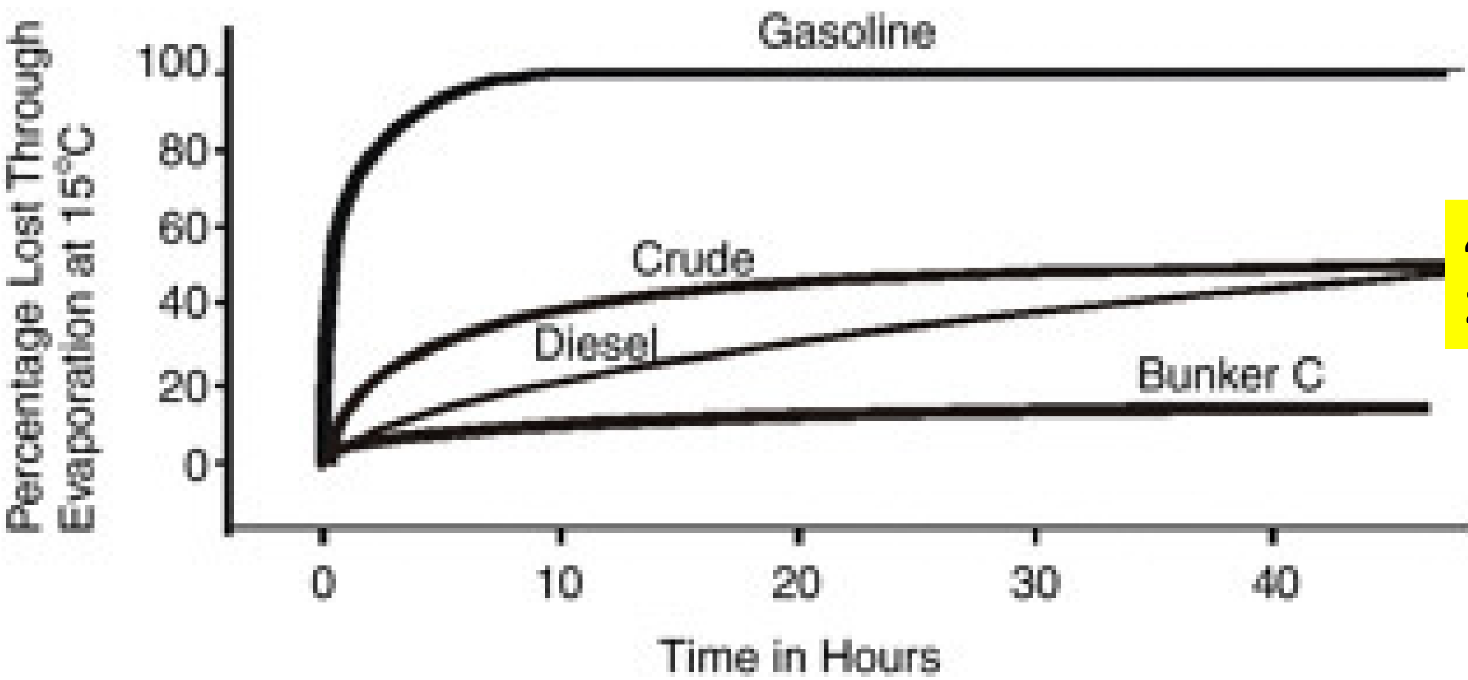
Spreading – depends on type/viscosity of oil, landscape slope/topography, soil type, which affects shape and spreading of oil on the surface (surface tension)

Penetration – depends on type of oil (light oils e.g. diesel), respective temperatures (hot oils penetrate more than cold), pore size and geology:

1. **Romania** (crude) 120 cm (many yrs)
2. **Saudi** (crude experiment) 10 cm/20 days
3. **Nigeria** (crude) Restricted soil sampling beyond 15 cm due to hard pan formation from crude oil and soil which constrained the study.
4. **Canada** (jet fuel spill) = 260 cm/12 hrs
5. **Colombia** = ?? cm

Sources: 1. Marinescu et al 2010. An assessment of the effects of crude oil pollution on soil properties. AFST 11(1): 94-99; 2. Benzagouta et al. 2011. Investigation on crude oil penetration depth into soils. Arabian J Geosciences; 3.   4. Grimaz et al 2008. Fast prediction of the evolution of o il penetration into the soil immediately after an accidental spillage for rapid-response purposes. Chemical Engineering Transactions. 13: 227-234

Type of Oil and Evaporation



40% in 2 days

Light crude

Source: © *Handbook of Oil Spill Science and Technology* 1st Ed. Ed. M. F. Fingas. 2015 John Wiley & Sons, Inc.

More Evaporation Rates

Medium crude

Table 1: Percentage weight loss from Burgan oil, Kuwait at selected temperatures and time with an flow of 1000 round/min

Temperature (°C)	8 h	Time 104 h	200 h
25	13.07	20.47	25.68
30	14.40	21.59	25.74
40	16.76	26.77	31.86
50	17.06	29.91	36.60

4 days

8 days

Table 2: Changes in density, API gravity and viscosity of the Burgan crude oil with progressing evaporation

Temperature (°C)	8 h	Time 104 h	200 h
Original oil	0.876	30	65.30
12.9	0.893	27	120.4
20.0	0.904	25	132.5
30.0	0.922	22	300.5

Source: Al Rashed Ahamad & Barker (2011) Role of Evaporation in Degrading the "Oil Lakes". *Am. J. Envir. Sci* 7 (3): 219-223.

Effects of Oil on Soil

Water/moisture movement – crust of asphaltine on surface, or layer of pore-filled oil – restricts vertical water movement, and soil can become hydrophobic (even after 43 years)*

Pore space – (as above) space filled with oil. No oxygen/air movement.

Organic carbon levels – increased, derived from the carbon in oil.

Germination and growth of plants – mostly highly negative. Plenty of examples from Nigeria, Romania, etc. Colombia?

Photo released by Petroecuador shows a 420,000-gallon oil spill in Ecuador's Amazonian region in June 2013. (AP Photo/Petroecuador)

* Gordonallan et al. 2018 *Geoderma* 312: 114-120.

Key messages

- Hydrocarbons are complex compounds with varied properties, but are dominated by hydrogen and carbon; properties are determined at the source of the crude.
- Once spilled, oil spreads, evaporates, disperses, and may emulsify; at the same time, weathering begins and the oil's physical and chemical properties change.
- Surface evaporation of volatile compounds can occur quickly, especially in warm climates, resulting in a thickened residue.
- The speed and process of weathering are important in determining response actions.

Thank you

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