

Soil Contamination By Spill And Leakage Hydrocarbons In Petroleum Refineries

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Abstract:

This study has been carried out on the soil that exposed to the contamination by hydrocarbons due to spill and leakage. Soil pollution with hydrocarbons has become an important problem of our days. When released on soil surface, petroleum hydrocarbons adsorb on the organic mineral matter of the soil. This paper presents the data obtained during the study achieved at three sites at Tobruk petroleum refinery of four horizons at depths of soil profile (0-20 cm, 20-30 cm, 30-40 cm and 40-50 cm). Each site represented a characteristic features of a definite soil e. g. sandy soil, calcareous soil and argillaceous soil. The pollutant is crude oil, and the main parameter followed is total petroleum hydrocarbons (TPH). The

concentration of TPH is varying from site to another and from depth to depth. This variation may be attributed to the soil type, soil texture, petrophysical properties and the main component of hydrocarbons.

The distillation fractions of the crude oil e.g. gasoline kerosene and diesel show variable retention capacity for the different soil types, where the lower retention capacity was recorded in coarse sand and the highest capacity in fine sand and clay.

Key words:

Soil contamination, crude oil, total petroleum hydrocarbon, spill, leakage, soil texture, concentration.

1. Introduction:

Currently, about 80% of lands are contaminated/polluted by products of petroleum origin (hydrocarbons, solvents etc.) used as an energy source in the oil industry, as well as chemicals. There is a variety of pollutants affecting soil and subsoil, such as fuel and oil products, hydrocarbon residues, crude oil, other products resulting from the operation (saturated and unsaturated aliphatic hydrocarbons, and the monocyclic and polycyclic aromatic).

Accidental oil pollution has become nowadays a common phenomenon that can cause environmental and social disasters [1]. Potential sources of direct pollution of soil and subsoil can be covered by tanks, separators old from wastewater treatment plants, settling basins, slurries and waste pits of tar, ramp CF loading and unloading, underground pipelines, sewerage networks etc.[2].

These types of products (mainly hydrocarbons) have a harmful risk, affecting the quality of groundwater, which becomes unfit for use for a

long time. It poses risks to human health, biological environment and vegetation, aromatic compounds having a strong feature of mutagenic and carcinogenic and, not least, affect the environment security, presenting risks of explosion and fire.

Spills and leaks are the most common accidents encountered at the production sites. The spill of condensate, oil or produced water onto the lease and the surrounding areas exhibits the greatest liability to the producer. Chemicals associated with operations may also leak and create an undesirable situation[3].

Soil contaminated by a spill or leak may be treated as an exempt waste provided the leaking substance is listed as an exempt waste. The hydrocarbon/soil mixture may be left in place provided that all petroleum products stay on location. In warmer climates the appearance of a sheen during runoff conditions may be apparent, thus increasing the likelihood of hydrocarbon contamination to the immediate area[4].

2. Material and Methods:

2.1. Soxhlet extraction:

Soil polluted samples were extracted for 24h by a Soxhlet extractor to yield the hydrocarbons. Soxhlet extraction, invented for the extraction of lipids from a solid material (von Soxhlet, 1879) is usually required when the desired extractable compounds have only a limited solubility in a solvent.

For the present study the polluted soil samples were filled inside a solvent pre-cleaned extraction thimble made from filter paper, which was placed into the main chamber of the Soxhlet extractor. The extraction pot was filled with 150 ml of solvent, a mixture of dichloromethane and

ethanol in ratio 99:1, and the solvent was heated to reflux. The solvent vapour travelled up a distillation arm, and flooded into the chamber housing the thimble of soil samples. The condenser ensured that any solvent vapour cooled and dropped back down into the chamber housing, where the source rock bitumen dissolved in the solvent mixture. When the Soxhlet chamber was filled up with solvent, the chamber was automatically emptied by a siphon side arm, with the solvent and dissolved hydrocarbons running back down to the distillation flask. This cycle was allowed to repeat over 24 hours.

As a result of a spill, a hydrocarbon may impose a hazard to groundwater, flora, fauna, and humans[4]. Hydrocarbon content in the soil in excess of the saturation limit may be transmitted to the surrounding environment through runoff and gravity. These hydrocarbons are loosely categorized as dense or light nonaqueous phase liquids. Hydrocarbon that may be retained by a volume of soil, the depth of infiltration is given in the following equations:

$$V_s = 0.2 V_{hc} / \phi S_r \quad (1)$$

where:

V_s = soil require to obtain residual saturation in yd^3

V_{hc} = volume of spilled hydrocarbon in bbl

S_r = residual oil saturation capacity of the soil

ϕ = soil porosity

and knowing the area of infiltration of the soil, the depth of the spill may be determined by:

$$D = 27V/A \quad (2)$$

Where:

D = depth in ft

A = observed area of infiltration in ft²

The case study achieved was necessary to establish the degree of pollution of the contaminated/polluted area with crude oil. The evaluation of total petroleum hydrocarbon (TPH) content with the horizons in the profile achieved at the three sites (I), (II), and (III) for sandstone soil, calcareous soil and argillaceous. The sites depths are 0-20 cm, 20-30 cm, 30-40 cm and 40-50 cm for each soil type. The obtained samples have been analyzed in the central laboratory of the refinery to determine the contamination levels in the different horizons of soils using different techniques.

3. Impact of hydrocarbons on the environment :

The specific effects of hydrocarbons on the environment differ depending on the type of hydrocarbons spilled and environmental conditions. The history of the hydrocarbons can also play a role. Used oils, waste oils and bilge slops may have different effects than fresh products.

Environmental conditions play a role in harm caused by hydrocarbons. Higher temperatures and/or winds create conditions resulting in faster evaporation of volatile products. Higher wind and wave conditions can mix water into some oils, creating a mousse that is more viscous (thick, sticky) which is more likely to cause mechanical injury. Environmental conditions such as air and temperature, wind speed, humidity, and direct sunlight .

Hydrocarbons have three main environmental impacts:

1. Acute (immediate) toxicity – A measure of the amount of volatile compounds in the oil that readily dissolve into water and are capable of killing plants and animals by poisoning. Inhalation of the volatile compounds in the air may also kill by poisoning.
2. Mechanical injury - A measure of how much harm oil causes to organisms and habitats due to its physical impact (coating, smothering).
3. Persistence - A measure of how long oil will stay in the environment before it breaks down.

The following are relative acute toxicity characteristics of various hydrocarbons in order of most to least toxic[5]:

1. Gasoline, Aviation Fuel (Av. Gas), and Naphtha contain high levels of volatile compounds (essentially 100% will evaporate) and are the most acutely toxic (lethal) petroleum products to organisms.
2. Jet Fuel, Kerosene, and No.1 Fuel Oil is intermediate in acute toxicity between gasoline and diesel (80% to 90% will evaporate).
3. Diesel Fuel, Home Heating Oil, and No.2 Fuel Oil contains some volatile compounds that are acutely toxic to organisms (50% to 70% will evaporate).
4. Crude Oil contains all components of refined petroleum products (except additives), including the volatile compounds and is acutely toxic to organisms during the early stages of a spill incident (30% to 40% will evaporate).
5. Lubricating Oils (grease, gear oil, motor oil, hydraulic oil, mineral oil) contain no volatiles and have low acute toxicity.

4. Persistence :

A measure of how long hydrocarbons stay in the environment before breaking down. Hydrocarbons with high persistence tend to foul habitats for longer periods and pose ongoing threats to organisms that rely on these habitats. Persistence is also a rough measure of chronic (long term) toxicity. Certain compounds in hydrocarbons can persist in the environment for months or years following a spill. Many oils have components called polycyclic aromatic hydrocarbons (PAH). Recent research indicates that some types of PAHs cause long term, sub-lethal, chronic effects to organism growth, reproduction, and survival. This can result in harmful effects to populations over time⁽¹⁾.

The following are relative persistence characteristics of various hydrocarbons from most to least persistent[5]:

1. Crude Oil is extremely persistent lasting five to ten years or more in the environment.
2. Lubricating Oils (grease, gear oil, motor oil, hydraulic oil, mineral oil) are moderately persistent lasting one to two years in the environment.
3. Diesel Fuel, Home Heating Oil, and No.2 Fuel Oil is somewhat persistent lasting one month to a year in the environment.
4. Jet Fuel, Kerosene, and No.1 Fuel Oil breaks down quickly, usually lasting only days to weeks in the environment.
5. Gasoline, Av Gas, and Naphtha breaks down very quickly, usually lasting only days to weeks in the environment.

Table 1 presents the relative environmental impacts of some petroleum products for acute toxicity, mechanical injury and persistence.

Table 1: Environmental impacts of hydrocarbons[5].

Hydrocarbons Class	Acute Toxicity	Mechanical Injury	Persistence
Gasoline, Av Gas, Naphtha	High	Low	Low
Kerosene, Jet Fuel, FO-#1	Medium	Medium -Low	Low
Diesel, Fuel Oil FO-#2, Heating Oil	Medium	Medium	Medium - Low
Bunker Fuel, FO-#6, IFO-380	Medium	High	High
Motor Oil, Hydraulic Oil	Low	Medium	Medium
Hot mix Asphalt	Low	Medium	High
FO – Fuel Oil IFO – Intermediate Fuel Oil			

In addition to these physical methods, chemical alterations and biotransformation are also used in site remediation. Table (2) shows a relative comparison between selected treatment techniques.

Table 2: Comparison of treatment processes[6]

Type of treatment	Time required (months)	Addition factors	Safety issues
Incineration	6-9	Energy	Air pollution
Fixation	6-9	Transport/monitoring	Leaching
Landfill	6-9	monitoring	Leaching
Biotreatment	18-60	Time	Intermediary metabolites and polymerization

5. Treatment Techniques:

5.1. Landfarming

Landfarming utilizes in situ and introduced microbes such as *Bacillus cereus*, *Bacillus polymixa*, *Arthrobacter globiformis* and *Acanigenes paradoxus* to degrade contaminants. Heterotrophic bacteria use organic compounds as energy and the carbon source for synthesis. The heterotrophs are classic oil spill degraders[7].

Autotrophic bacteria use carbon dioxide as a carbon source and oxidize inorganic compounds for energy. They are most useful in drilling mud degradation. In some instances biodegradation of contaminants may result in harmful intermediates, as with mercury. Mercury and other minerals, in their pure metal form, may remain immobile until the introduction of reducing microbes. The altering of conditions, pH and organic content, may change the redox state of the metal. Under such conditions, the metal may then be prone to migration and thus be leached into the groundwater. Also, anaerobic microbes may reduce the metal to a sulfide whereby solubility is enhanced[8].

In the case of oil spills, on-site bioremediation has proven successful. In situ microbial strains are active in most soils[9].

5.2. Landspreading:

Land spreading is differentiated from landfarming in that the area over which the contaminated soil or liquid is spread is not actively manipulated to increase degradation rates. One study showed that by spreading oil-based cuttings over an area of soil at thicknesses not over 2 in. has led to natural degradation rates of approximately 80% in the first year and 95% of the hydrocarbons had been eliminated after 3 years. Further analysis proved no significant migration or leaching of the

hydrocarbons had taken place[10]. Another method of landspreading includes reliquidifying the solids and then spreading them evenly over an area. Here, the loading factors take into consideration the soil and contaminant characteristics[11].

5.3. Airstripping:

In phase transformation, most often the liquid phase is let to a gaseous phase, through the addition of heat, a reduction in pressure or concentration, or any combination thereof[12]. Evaporation may be used as applied through variations of Equation (3). The two film theory states the basis for most air stripping operations, and is mathematically defined by:

$$\frac{dC}{dt} = -K_L a (c_a - c_t) \quad (3)$$

where :

C = concentration of the hydrocarbon in M

$K_L a$ = overall rate constant in hr^{-1}

C_a = concentration of the hydrocarbon in the gas phase at time (t) in M

C_t = concentration of the hydrocarbon in the liquid bulk at time (t) in M

6. Results and Discussion

The evaluation of total petroleum hydrocarbon (TPH) content with the horizons in the profile achieved at the three sites (I), (II), and (III) for sandstone soil, calcareous soil and argillaceous soil show variable concentrations as following:

In site (I) made on 4 horizons depths for sandstone soil was registered the highest concentration of total petroleum hydrocarbons with a value by 5020 mg kg^{-1} on 40-50 cm depth, followed by 4750 mg kg^{-1} on

30-40 cm depth, 4050 mg kg⁻¹ and at surface (0-20 cm) and 3150 mg kg⁻¹ (Fig. 1).

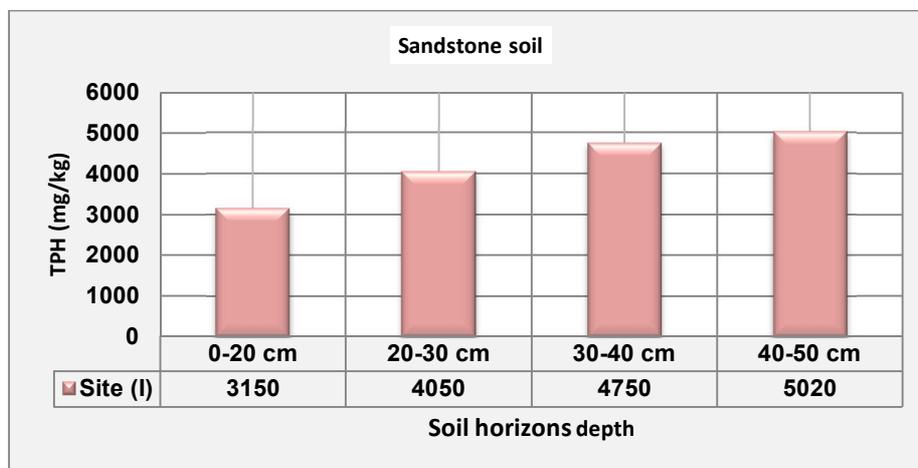


Fig. 1: Evaluation of TPH content in the profile achieved at site (I) of sandstone soil

In site (II) for calcareous soil the concentration of total petroleum hydrocarbons exhibits variable content in this type of soil, where the highest concentration with a value 5300 mg kg⁻¹ on 0-20 cm was recorded at surface, while the other horizons show lower contents (Fig. 2).

In site (III) for argillaceous soil the concentration of total petroleum hydrocarbons show high content in horizons 40-50 cm (6200 mg kg⁻¹) and 20-30 cm (6150 mg kg⁻¹) as shown in Figure 3.

The variation in content of TPH in the three soil may be attributed to their different types, their different textures and petrophysical properties.

The hydrocarbons products retention capacities in unsaturated soils represented by gasoline, kerosene and diesel had been examined in different soil types of different textures e. g. gravel, coarse sand, coarse & medium sand, medium & fine sand and fine sand & clay.

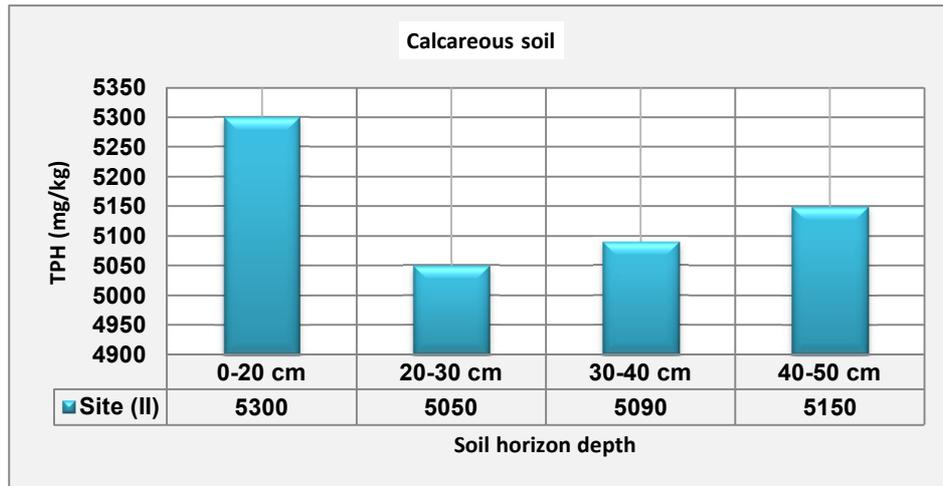


Fig. 2: Evaluation of TPH content in the profile achieved at site (II) of calcareous soil

The hydrocarbons products show some variation in their retention capacities for the different soil types. Gasoline exhibits the highest retention capacity in fine sand and silt (55 l/m^3) and the lowest retention capacity in gravel (10 l/m^3) as shown in Figure 4.

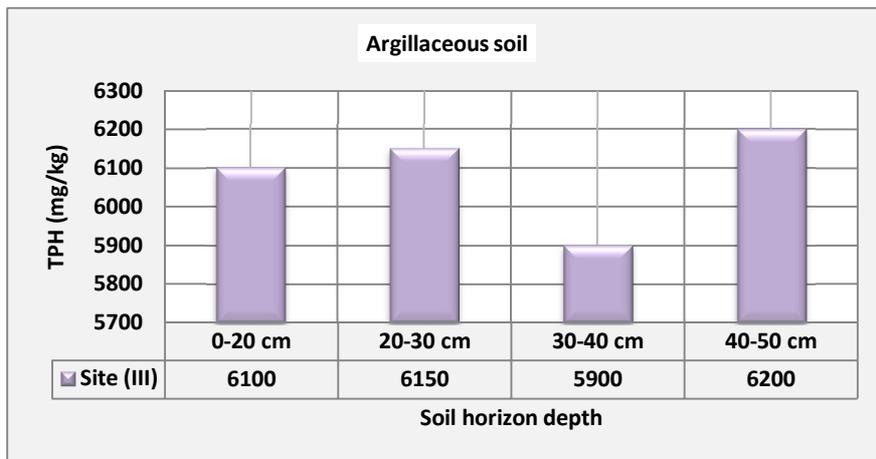


Fig. 3: Evaluation of TPH content at site (III) for argillaceous soil

Also, the same case for both kerosene and diesel with different retention capacities ranging from 5 to 39 l/m³ and 10 to 44 l/m³ respectively (figs. 5 & 6). This may be attributed to the soil type and soil texture as well as hydrocarbon products.

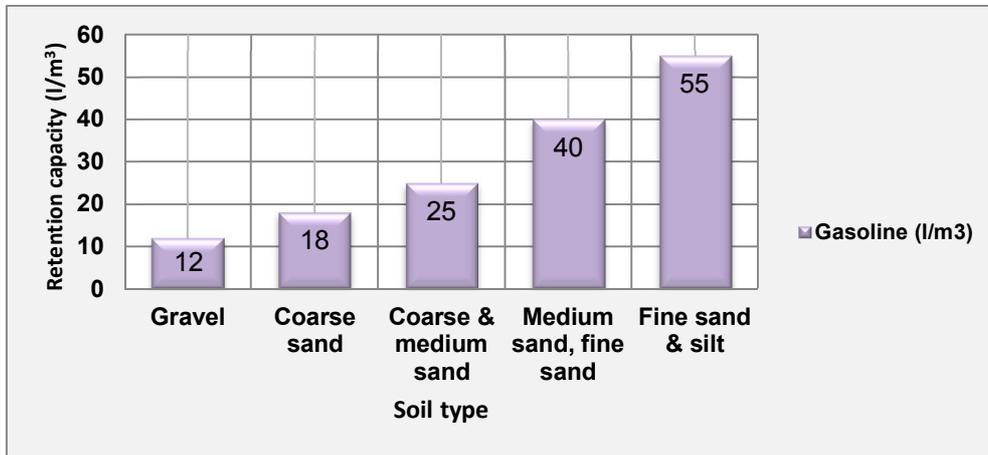


Fig. 4: Retention capacities of gasoline in different soil types

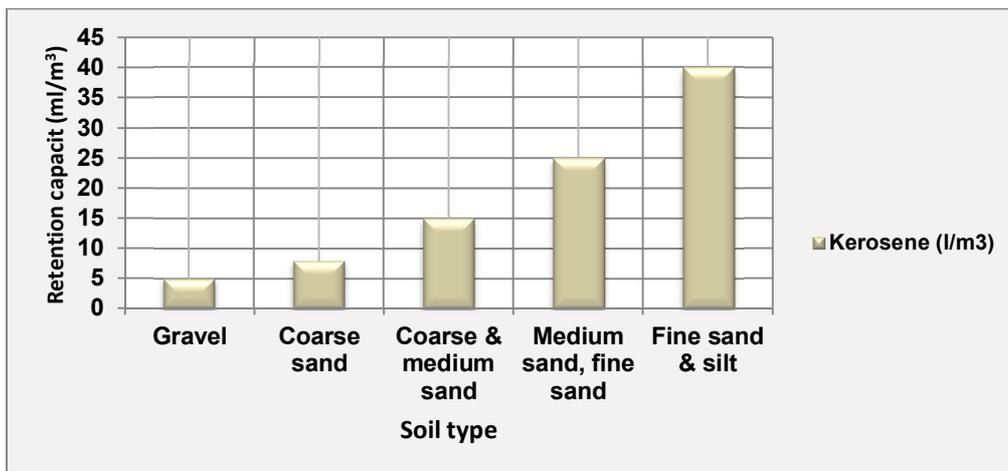


Fig. 5: Retention capacities of kerosene in different soil types

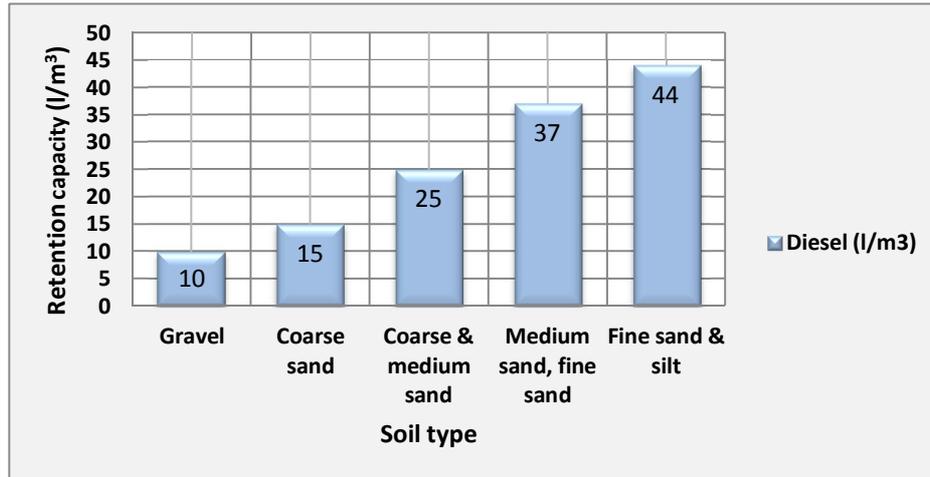


Fig. 6: Retention capacities of diesel in varieties of soil

7. Conclusion:

The study was achieved in petroleum facilities known for petroleum hydrocarbons pollution by spill and leakage.

The evaluation of total petroleum hydrocarbon (TPH) content in soil with the horizons in the profile achieved at the three sites (I), (II), and (III), for sandstone soil, calcareous soil and argillaceous soil respectively show variable concentrations. The pollution degree of the studied sites is excessive in the majority of the soil samples.

In site (I) made on 4 horizons depths for sandstone soil was registered the highest concentration of TPH with a value by 5020 mg kg⁻¹ in the lower horizon (40-50 cm).

In site (II) for calcareous soil the concentration of TPH exhibits variable content in this type of soil, where the highest concentration with a value 5300 mg kg⁻¹ on 0-20 cm was recorded at surface, while the other horizons show lower contents.

In site (III) for argillaceous soil the concentration of TPH show high content in horizons 40-50 cm (6200 mg kg^{-1}) and 20-30 cm (6150 mg kg^{-1}).

The variation in content of TPH in the three soil may be attributed to their different types, petrophysical properties, their different textures and the main component of hydrocarbons.

The hydrocarbons products retention capacities in unsaturated soils represented by gasoline, kerosene and diesel had been examined in different soil types of different textures e. g. gravel, coarse sand, coarse & medium sand, medium & fine sand and fine sand & clay. They show some variation in their retention capacities for the different soil types. Gasoline exhibits the highest retention capacity in fine sand and silt (55 l/m^3) and the lowest retention capacity in gravel (10 l/m^3). Also, the same case for both kerosene and diesel with different retention capacities ranging from 5 to 39 l/m^3 and 10 to 44 l/m^3 respectively. This may be attributed to the soil type and soil texture as well as the nature of hydrocarbon products.

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