

# Fate of Subsurface Migration of Crude Oil Spill: A Review

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## 1. Introduction

The sensitivity of crude oil operational areas and the devastating effect of crude oil spillage on the lithosphere, biosphere, hydrosphere and atmosphere is established fact. The impacts of these spills on the ecosystem leave indelible imprints. While literature abounds on studies involving the collection of baseline data and the prediction of effects using expert judgments, experiments, interviews and models, mitigation and control measures to minimize the impact has recorded limited success over the years.

With research still in progress on ways and means to handle ecological crude oil pollution when they occur, including the search for alternative energy resources, reviews on the knowledge and understanding of the interaction of crude oil spill and the environment must remain essential. This will help to foster and evolve the much needed solution to better effective mitigation and control strategies and hence ensure a sound and sustainable environment.

Pollution occurs when the concentration of various chemical or biological constituents exceed a level at which a negative impact on amenities, the ecosystem, resources and human health can occur. Pollution results primarily from human activities (Awobajo, 1981).

The sources of pollution include sewage, urban run-off, industrial processing wastes and effluents, coastal developments, shipping activities and atmospheric dust and fall out. The chemical or biological constituents creating pollution are known as contaminants. Contaminants degrade the natural quality of a substance or medium. Inorganic contaminants include zinc, lead and pesticides. Organic contaminants consist of petroleum hydrocarbons and biological pollutants (coliform bacteria and pathogens).

Petroleum as the contaminant or pollutant of interest here is a complex mixture of naturally occurring hydrocarbons in the solid (Asphalt, pitchblende, tar), liquid (crude oil) and gaseous state (natural gas). It is a mixture of hundreds of hydrocarbons highly variable in composition whose individual chemical properties vary widely. Its properties depend on the properties of the individual constituents and is made up basically of paraffin, aromatics, asphalt and naphthenes.

Petroleum deposits contain similar elements, usually 11-15% Hydrogen and 82-87% Carbon. Some of the compounds are more amenable to volatilization than to dissolution, and vice versa. Also, other components within petroleum are not particularly prone to either and will tend to persist in the subsurface (Webb, 1985).

Petroleum products fall within the class of liquids that do not readily dissolve in water and can exist as a separate fluid phase known as non-aqueous phase liquids (NAPLs). It is also known to be lighter than water and sub-grouped as LNAPLs. Those with a density greater than water (DNAPLs) are chlorinated hydrocarbons such as carbon tetrachloride and chlorophenols (Palmer and Johnson, 1989).

Non-aqueous phase liquids (NAPLs), such as petroleum, chlorinated solvents and polychlorinated biphenyl (PCB) oils, are a common cause of groundwater contamination in many industrialized countries (Keely, 1989).

Although these liquids exist as a separate fluid phase in the subsurface, they typically have solubilities orders of magnitude greater than drinking water standards.

Predicting the fate of these chemicals in the subsurface is a challenging problem that needs to be addressed at many sites, before an effective remediation result can be achieved.

## 2. Evaluation of physical transport parameters

Access to and the utilization of knowledge about contaminant transport and fate is difficult because of the complexity of the sub-surface environment. Furthermore transport and fate assessments require inter-disciplinary analyses and interpretations because the process involved in these activities are naturally intertwined (Keely, 1989).

The integration of information on geologic, hydrologic, chemical and biological processes into an effective contaminant transport evaluation requires data that are accurate, precise, and appropriate. Even though a given parameter, such as hydraulic conductivity, can be measured correctly and with great reproducibility, it is difficult to know how closely an observation actually represents the vertical and horizontal distribution of conductivities found at a site.

It is important to appreciate the processes involved in the transport of contaminants in both porous and fractured media under saturated or unsaturated conditions. This information will assist in the design of efficient and cost-effective monitoring networks and remediation strategies of ground and surface water resources.

The severity of soil contamination tends to be a function of the properties of the soil. Knowledge of the infiltration process is prerequisite for managing contaminant transport in the unsaturated or vadose zone (Fig.1). The vadose zone is the area between the surface of the land and the aquifer water table in which the moisture content is less than the saturation point and the pressure is less than atmospheric. Depth of the vadose zone varies greatly, depending on the region of the site. Because the vadose zone overlies the saturated zone, chemical releases at or near the land surface must pass through the vadose zone before reaching the water table. The depth to the water table which is equivalent to the thickness of the unsaturated zone, is one of the parameters that determine whether or not a pollutant will reach the water table from a surface spill. Therefore, at many contaminated sites, often

both the vadose zone and the saturated zone need to be characterized and remediated (Mercer and Spalding, 1989). The unsaturated zone is an integral component of the hydrological cycle, which directly influences infiltration. Infiltration is defined as the initial process of water (or contaminant) movement into unsaturated zone through the soil surface (Tombul, 2003). The maximum rate at which fluid can move into the soil is called the infiltration capacity or potential infiltration rate (Bouwer, 1978).

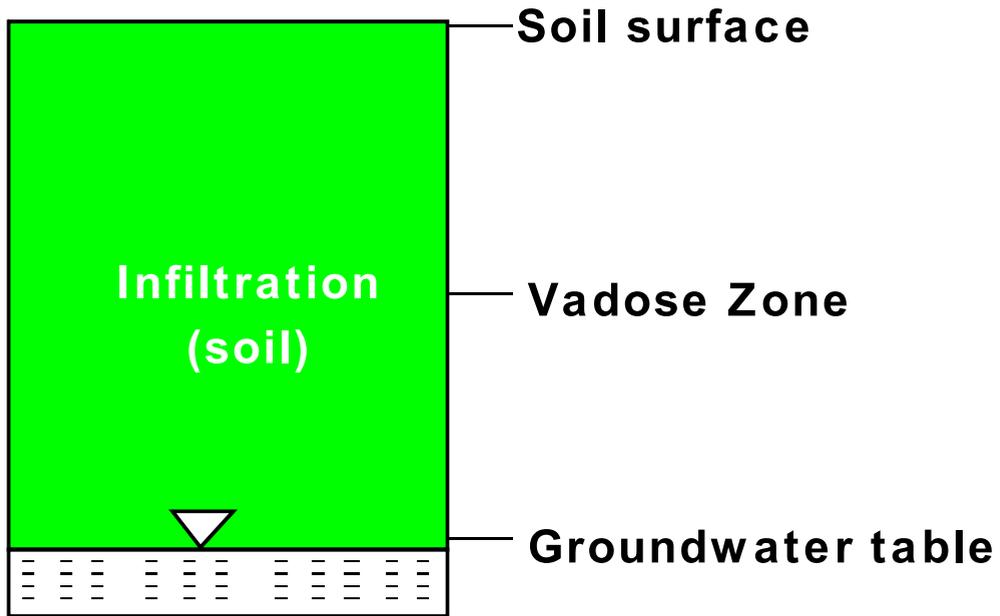


Fig. 1. Typifying the Vadose Zone

The ability to transmit fluid or the hydraulic conductivity of the soil is a highly variable quantity. If the soil is composed of well-sorted sand or gravel, the conductivity will be high and will vary only slightly with time. Most natural sediments, however, develop a stratified structure. As a result of their depositional history, the hydraulic properties (permeability, porosity etc.) in the Formations are mostly heterogeneous and anisotropic. In a homogeneous sediment, porosity and permeability are equal everywhere.

Geologic heterogeneities within the Formations make it difficult to precisely quantify the hydrogeologic system and the resulting properties affecting contaminant transport. Groundwater flow or solute (pollutant) transport at a given location depends on the permeability of the subsoil and the potential or hydraulic gradient. Effective hydraulic conductivity or permeability is an important parameter for the prediction of infiltration and run-off volume of fluids. The ability of sediments to hold and transmit fluids is determined by their porosity and permeability. The porosity of a soil or rock material is the percentage of the total volume of the material that is occupied by pores or interstices; or simply the percentage of pore spaces in the material. These pores may be filled with water if the material is saturated or with air and water if it is unsaturated.

The facility of fluid flow through any porous medium is termed permeability. Any material with voids is porous and, if the voids are interconnected, possesses permeability. Permeability or hydraulic conductivity is also the ability of a soil to conduct or discharge water under a hydraulic gradient. It depends on soil density, degree of saturation, viscosity and particle size. Materials with larger void spaces generally have larger void ratios, and so, even the densest soils are more permeable than materials such as rocks and concrete. Materials such as clays and silts in natural deposits have large values of porosity (or void ratio) but are nearly impermeable, primarily because of their very small void sizes. Since natural subsurface geology is very heterogeneous, there can be various sizes of hydraulic conductivities in a relatively small area (Miller and Hogan, 1996). Permeability vary strongly for different sediments, but porosities vary only from values of 0.2 (20%) for coarse, unsorted sands to 0.65 (65%) for clay (Bowles,1985).

### 3. Contamination characterization

The fate of hydrocarbons in the subsurface depends on the processes of transport, multiphase flow, volatilization, dissolution, geochemical reactions, biodegradation, and sorption (Figure 2). An interdisciplinary investigation of these processes is critical to successfully evaluate the potential for migration of hydrocarbons in the subsurface.

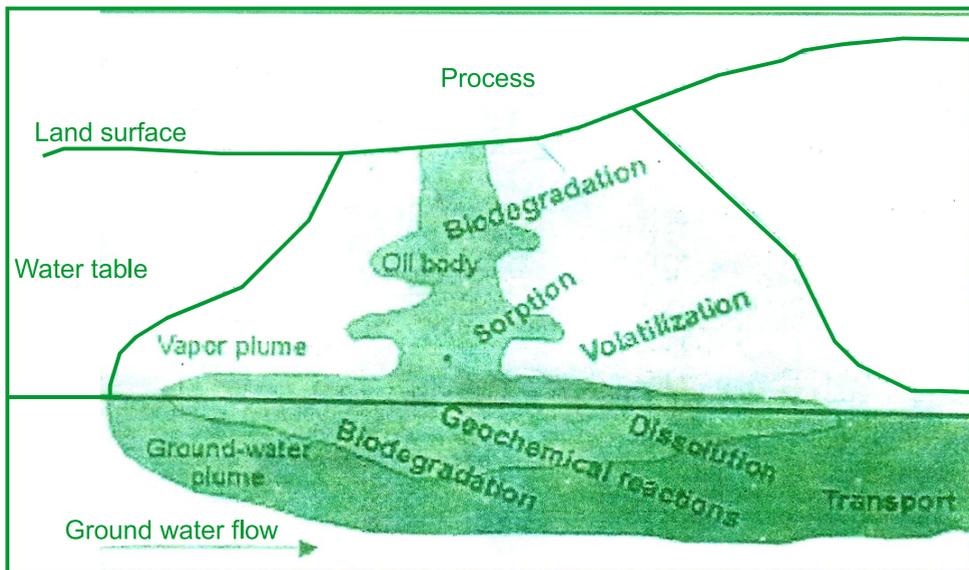


Fig. 2. Processes critical to understanding the fate and transport of hydrocarbons In the subsurface.

Contaminant transport in the subsurface is affected by different processes. They include advection, dispersion, diffusion, adsorption and decay. These processes can work together or separate in groundwater flow (Miller and Hogan, 1996).

The process by which contaminants are transported by the bulk motion of the flowing groundwater is known as advection. Non-reactive solutes are carried at an average rate equal to the average linear velocity,  $V$ , of the water (Freeze and Cherry, 1979). The average linear velocity,  $V$ , at which groundwater flows through a porous aquifer is given from the modified Darcy relations:

$$V = -\frac{K}{n} \frac{dh}{dL} \quad (1)$$

Where  $K$  is the hydraulic conductivity of the formation in the direction of groundwater flow,  $n$  is the porosity of the formation and  $dh/dL$  is the hydraulic gradient in the direction of groundwater flow.

Dispersion is a mixing process. According to the advective hydraulics of flow system, the solute has the tendency to spread out from its flow path by a spreading phenomenon called hydrodynamic dispersion, which causes dilution of the solute. Hydrodynamic dispersion is the combined effect of mechanical dispersion and molecular diffusion (Mercer and Spalding, 1989). Freeze and Cherry (1979) states that it occurs because of mechanical mixing during fluid advection and because of molecular diffusion due to the thermal-kinetic energy of the solute particles. Mechanical dispersion is the mixing of the contaminant resulting from movement through complex pore structures (Greenkorn, 1983) and is due mainly to the porous medium. Mechanical dispersion is predominant at high groundwater velocities while, molecular diffusion is significant at low velocities.

When a contaminant is diluted in the groundwater it follows the path of normal flow and is called lateral dispersion. Due to heterogeneities in soil particle size and pore size, dispersion will occur.

Freeze and Cherry (1979) defines longitudinal dispersion as the spreading of solute in the direction of bulk flow. Spreading in directions perpendicular to the flow is called transverse dispersion. Longitudinal dispersion is normally much stronger than lateral dispersion and is the process whereby some of the water molecules and solute molecules travel more rapidly than the average linear velocity and some travel more slowly. The solute therefore spreads out in the direction of flow and declines in concentration. Dispersion coefficient varies with the groundwater velocity and is relatively constant at low velocities, but increases linearly with velocity as the groundwater velocities increase.

The study of dispersion phenomenon is important for predicting the time when a concentration limit used in regulations such as drinking water standards, will be reached and for determining optimal, cost-effective strategies for aquifer remediation (Palmer and Johnson, 1989).

Molecular diffusion is due to concentration gradients and the random motion of molecules (Miller and Hogan, 1996). Diffusion does not need advective velocity to occur. It is a process due to the contaminant alone. The larger the amount of pollutants the greater and farther the effects of diffusion can be. It is usually found to have effects at low velocities or long

time periods of travel. Diffusion is a dispersion process of importance only at low velocities. Formation that is dependent on diffusion would be a low hydraulic conductivity layer. These layers will have such low velocities regular dispersion will not be noticed.

According to Mercer and Spalding (1987), adsorption is the transfer of contaminants from the groundwater to the soil. Desorption is the transfer of contaminants from the soil to the groundwater. These processes involve mass transfer of contaminants. Adsorption is also the ability of a compound to "attach" itself to the soil (Miller and Hogan, 1996). It is dependent on the properties of the soil and the compound. Differences in solubility and reaction with organic materials help make up a wide range of adsorption strengths.

Decay or degradation is the biological decomposition or chemical alteration of dissolved compounds. Miller and Hogan (1996) stated that decay does not affect how fast or how far pollutants will travel. Biological or chemical processes will reduce the amount of compounds traveling through the system but the effects of advection will stay the same. Processes that involve mass transfer of contaminants by chemical reactions will include precipitation and dissolution, oxidation and reduction while biological transformation may remove contaminants from the systems by biological degradation, or transform contaminants to other toxic compounds that are subject to mass transfer by the other processes earlier discussed.

The processes of adsorption-desorption, chemical reactions, and biological transformation play important roles in controlling the migration rate as well as concentration distributions. These processes tend to retard the rate of contaminant migration and act as mechanisms to reduce concentrations (Mercer and Spalding, 1989). Crude oil that is fairly viscous, with a high wax content and high pour point will have slow rates of spreading and dispersion (Webb, 1985). Generally, the rate of hydrocarbon loss due to evaporation is high during the early states of a spill, which renders the oil less toxic and less flammable. Evaporation results in an increase in oil viscosity and density, which further retards the spreading rate.

#### **4. Fate of crude oil spill pathways**

Naturally formed soil profiles are rarely homogenous with depth, rather they contain distinct layers, or horizons with specific hydraulic and physical characteristics. Because migration depends on subsurface lithology, the presence of these layers in the soil profile will generally retard water and contaminant movement during infiltration (Tombul 2003). Clay layers will impede flow due to their lower saturated hydraulic conductivity. However, when these layers are near the surface and initially very dry, the initial infiltration rate may be much higher and then drop off rapidly. Hult and Grabbe (1985) observe that as crude oil moves from a spill site, it contaminates soil in the vadose zone since its components are largely water insoluble and less dense than water, hydrocarbon free product tends to reside and spread along the water table boundary. Hydrocarbon free product can easily pollute wells within the zone of contamination, and also can sorb to and contaminate those soil areas influenced by water table fluctuations. This sorbed material tends to be another more subtle source of secondary contamination. In addition, free product can contaminate surface waters, and hydrocarbon vapors can collect in basements of buildings and create inhalation or explosion risks.

It was observed that vertical hydraulic gradients exist between some zones at some study sites. These gradients would physically provide the vertical hydraulic force necessary to transport light-non-aqueous phase liquids (LNAPLs) such as crude oil through the various water-bearing zones (Mercer and Spalding, 1989). Vertical migration proceeds until the interface between the unsaturated zone and saturated zone is met. At this point, free phase solvent would either spread laterally, continue through the water table vertically as DNAPL, or a combination of both. Because advection and dispersion are the primary transport mechanisms for LNAPLs (Miller and Hogan, 1996), horizontal (lateral) transport of LNAPLs within the Formation may likely occur through advection and dispersion within the shallow, intermediate and deep water-bearing zones at the study sites. Movement will be predominantly in the direction of groundwater flow through advection.

Density and solubility are among the primary physical properties affecting the transport of separate phase liquids in the soil and water. The density of a slightly soluble compound will determine whether it will sink or float in the saturated zone (Tombul, 2003). In some cases, dissolved concentrations are large enough that the density of the contaminant plume may contribute to the direction of solute transport. The contribution of density to the vertical component of groundwater  $V_g$ , can be calculated using the concept of equivalent freshwater head (Frind, 1982) by:

$$V_g = -\frac{K_v}{n} \left( \frac{p-1}{p_0} \right) \quad (2)$$

Where  $K_v$  is the conductivity in the vertical direction,  $n$  is porosity,  $p$  is the density of the contaminated water and  $p_0$  is the density of the native groundwater. According to Freeze and Cherry (1979), except for small amounts of hydrocarbons that go into solution, oil does not penetrate below the water table (oil is immiscible in water and is less dense). As oil accumulates on the water table, the oil zone spreads laterally, initially under the influence of gradients caused by gravity and later in response mainly to capillary forces. Capillary spreading becomes very slow and eventually a relatively stable condition is attained.

In theory, stability occurs when a condition known as residual oil saturation or immobile saturation is reached. Below a certain degree of saturation, oil is held in a relatively immobile state in the pore spaces. If the percent oil saturation is reduced further, isolated islands or globules of oil become the dominant mode of oil occurrence. Over the range of pressure gradients that can occur, these islands are stable. As the mass of oil spreads laterally due to capillary forces, the residual oil saturation condition must eventually be attained, provided that the influx of oil from the source ceases. This is referred to as the stable stage.

Degradation is the biological decomposition or chemical alteration of dissolved compounds (Awobajo, 1981). Biodegradation plays an important role in the fate of crude oil. Many components of petroleum are readily degraded by subsurface micro-organisms (Hult and Grabbe, 1985). In the saturated zone, biodegradation frequently makes the aquifer anaerobic, resulting in much slower rates of degradation. In the unsaturated zone, vapor-phase molecular diffusion can maintain an oxygen supply at distances below the ground surface (Hult and Grabbe, 1985). Palmer and Johnson (1989) note that the unsaturated or vadose zone often contains greater amounts of organic matter and metal

oxides than the saturated zone. Contaminants can adsorb onto these materials, making their rate of movement substantially less than in the saturated zone. Materials adhering to these absorbents can act as a source of contaminants to the saturated zone even after remediation.

The activity of the micro-organisms in the vadose zone generally is considered to be much greater than below the water table.

Furthermore, the unsaturated portion of the vadose zone can be a pathway for the transport of gases and volatile organics. These characteristics of the vadose zone can be important when predicting the transport of contaminants and designing systems for remediation. Hydrogeological studies are essential to underscore the fate of contaminant transport in the subsurface and the processes that govern them, such as advection, dispersion, diffusion, adsorption and decay. Its goal is also to determine the directions of groundwater flow at the polluted sites which information is essential to any groundwater remediation or monitoring program. The determined depth-to-water table (thickness of the unsaturated zone) is one of the hydrogeological parameters that determines whether or not a pollutant will reach the water table from a surface spill. High water table conditions will ensure that contaminant motion will be more of a lateral than vertical flow pattern. After the pollutants may have impacted the groundwater, it will tend to move laterally along these pathways, with its concentration decreasing as it moves away from the point or line sources of pollution due to dispersion and other attenuation effects, such as biological decomposition of organic compounds and precipitation of dissolved chemicals (Bouwer, 1978).

## **5. Ecologic-lithospheric sensitivity of crude oil spill**

Sensitivity index is essentially a geomorphological classification and relates to the sensitivity of a particular area. Geomorphology and related physical processes govern the deposition and persistence of oil in the environment. The Mangrove swamp is a peculiar sensitive environment; its soils consist mainly of clays, shales, clayey shales, organic silts, organic silty clays and frequently peat materials. The soils contain abundant organic matter and iron compounds, and bacterial decay is active (Hutchings and Saenger, 1987). The most commonly occurring soil type in the mangrove environment is the peaty silty clayey mud which is noted for its very high water absorbing capacity. The dense network of rivers and creeks, low ground elevation and negligible gravity drainage ensure shallow depth to groundwater in this environment. There is also dense vegetation typical of a brackish environment. These characteristics of the mangrove zone tend to enable it retain oil pollution in its system so that pollutants experience longer residence period in the environment (Saenger et al., 1983). As a result, mangrove swamps have been found to be the most sensitive environment that could be affected by an oil spill over time (Hutchings and Saenger, 1987). The saturated, anaerobic nature of the mangrove zone will also result in slower rates of crude oil degradation (Hult and Grabbe, 1985).

The mangrove swamp zone, by virtue of its characteristic geomorphology, lithology, drainage condition and vegetation is identified as having a peculiar sensitivity to crude oil pollution, as a result of the long residence period it exhibits over time to contaminants.

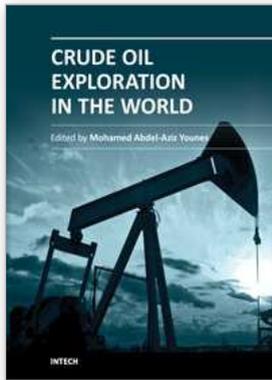
## 6. Discussion

The information revealed by this review is further pointer to the need for all remediation technologies to consider where the contaminants reside in the subsurface. It is important to appreciate the processes involved in the transport of contaminants in both permeable and non-permeable media under saturated conditions. The environmental sensitivity ranking of the polluted sites will also serve as guide to identifying the geomorphologic zones most susceptible to crude oil pollution. This information will assist in the design of efficient and cost-effective monitoring networks and remediation strategies of the soil, ground and surface water resources.

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