Cleanup of Oil and Chemical Spills

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There is no easy way to clean up an oil or chemical spill, just some less difficult ways, and the cleanup is never complete because one cannot clean it all up, just the fractions one can reach. Oil is not one compound, it is a mixture of several compounds, everything from highly volatile fractions such as ethylene and benzene to much heavier and stable compounds including asphaltenes. Some compounds float and evaporate, other fractions are heavier than water and sink. What differentiates an oil from a chemical spill is the fact that one cannot write a chemical equation for an oil spill because of the many different compounds in it.
There are several several types of oils, including vegetable oils, (soy bean oil, corn oil) etc. which each have their own specific properties. They are outside the principal scope of this article because they are refined oils, and their quantities in production and transportation with respect to petroleum oils is very low.

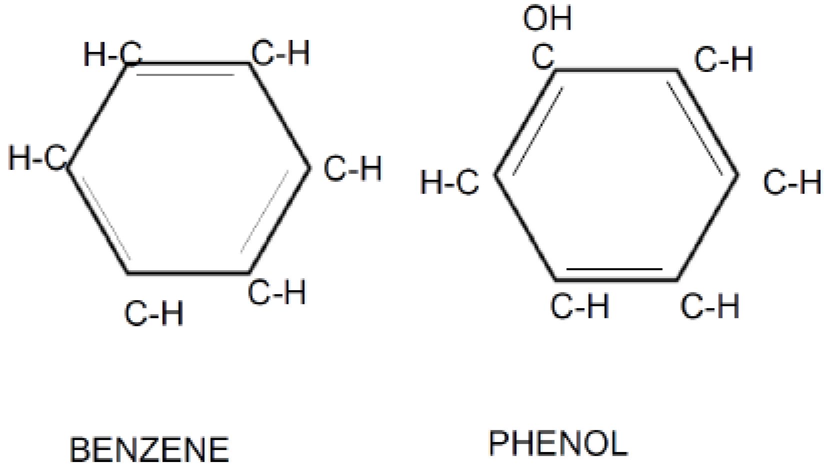
1 Petroleum Oils

The composition of petroleum oils is approximately as follows:

Compound	**Relative Composition**
Carbon	84-85%
Hydrogen	14-15%
Sulfur	1-3% in various forms (disulfides, H2S, S, etc.)
Oxygen	LESS THAN 1% in associated compounds such as CO2, Carboxylic Acids, etc.)
Nitrogen	LESS THAN 1% mostly in amine groups (compounds with NH3 groups)
Salts	LESS THAN 1% generally as chloride compounds of Sodium, Calcium, and Magnesium
Metals	Some small quantities (<1%) of Arsenic, Copper, Iron, Nickel, and Vanadium[i].

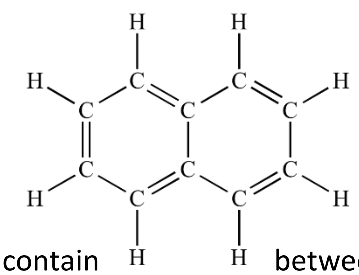
There are a number of chemical compounds in crude oil:
Paraffins have the general formula C_nH_{2n+2}, where n is a number from 1-22, and are between 15 and 60% of the total weight of crude oil. Paraffins are straight chain hydrocarbons such as methane, ethane, propane, pentane and hexane.
Aromatics have the general formula of C_6H_5-X, where X is a straight chain paraffin compound. Benzene rings are 6 carbon hexagons, but Aromatics may contain several benzene rings as well as any number of paraffins in the X portion. Examples consist of benzene, naphthalene, phenol, cyclohexane, and other compounds. Crude oil can consist of up to 30% of aromatic compounds

Figure 1. Structure of two aromatic compounds found in oil



Naphthalenes are ring structures of 6 carbons, often found in multiple rings, and have the general formula of C_nH_{2n} where n is a number less than 20. In adjacent rings, with either one or two bonds, the approximate formula is $C_nH_{2(n-4)}$ for adjacent rings connected at two points. Example: Naphthalene has a basic structure as shown below:

Figure 2. Chemical Structure of Napthalene



Naphthalenes are generally liquid at room temperature. Examples include cyclopentane, naphthalene (moth balls), and other compounds. Crude may contain between 30% and 60% naphthalene.

Asphaltics are heavier residual chemical compounds, generally solid at room temperature and very stable. Their chemistry is complex, and the compounds are often denser than water. One use of refined asphaltics is asphalt (road paving material). The quantity of asphaltics varies widely because they are residual products. They are often cracked (have their chemical bonds broken in refining) to provide lighter fractions which are used in various oils.

Many dense crude oil compounds are often emulsified in water – including Napthalenes and Asphaltics, and can

form a deposit on anything which they contact. They are also slow to biodegrade and have moderate to severe toxicity toward aquatic life. The deposits from the heavy oil fractions often form a coating or film on spill control booms, overbalancing them, and rendering them less effective. When the emulsified oil compounds hit beaches or plant life in wetlands, they adhere to the plant life, sand, and rocks, enter the interstitial spaces in the sand grains, crevasses and pores in the rock, and coat and plug the soil pores in the soils. The oil also forms layers in sand and soils which are difficult to remove without excavation of the sand and washing it with hot water and detergents, removing plant nutrients and associated micro-life.

The viscosity of crude oils further complicates the issues surrounding cleanup of spills. Crude oils are noted for their high viscosity[ii]. The viscosity of many crude oils is 100 or more times that of water at ambient sea temperatures.[iii] The following table illustrates some typical viscosities for household products[iv].

Table II. Common Viscosities of household substances

Material	**Viscosity in Centipoise**
Water at 21^{o}C	4
Ethylene Glycol – antifreeze	15
Corn Syrup	60-110
30 weight motor oil or Maple Syrup	150-100
Chocolate Syrup	10,000-25,000
Catsup or Mustard (yellow)	50,000-70,000

The higher viscosities of crude oils and certain chemicals complicate the clean-up and recovery effort, as do colder temperatures. Some products, such as No. 6 (or Bunker C) oil are so viscous it is semi-solid at 40^{o}C, and it has to be heated to over 100oC in order to pump it for transportation uses.

2 Absorbing the Spill

For some small spills, absorbent pads are used for cleanup. Absorbent pads are a cross between a paper towel and a sponge, and are often hydrophobic so they would not absorb water but would absorb oils. The pads come in sheets, rolls, blankets or pillows and long barrier pads. All those designed for marine or water applications are less dense than water and float. Many of the products have a specific oil capacity listing – a number estimating how much oil that particular product can absorb. There are also pads and products for non-oil spills.

For small spills, a few gallons, up to a few hundred gallons, on impermeable surfaces, these pads are invaluable. When placed on a spill, they grab the oil and hold it in the cloth where it can be recovered by wringing out the cloth. Most commonly, however, the pads are thrown away along with the recovered oil because of the intensive labor needed for reclamation. Absorbent materials require handling, both for application, collection, and disposal.

Exposure to oils and chemicals should be avoided. Personnel safety of cleanup crews should be important. Safety equipment used in cleanup of spills includes: impermeable gloves, protective suits (splash suits of Tyvek or other selected materials), goggles, boots, a life vest (for offshore work) and where appropriate a face mask with an organic vapor cartridge(s). Decontamination of personnel after collection is also strongly recommended, as boots, gloves, and protective gear can become coated with layers of sticky oils or clothing can be contaminated with chemical compounds.

Some manufacturers package spill control containers which contain supplies ready for deployment. These containers come in 30 and 55 gallon drum sizes, and contain pads, rope, and other barrier materials. One of the important barrier materials for industrial and in-plant uses is a magnetic drain cover. One element of effective spill control is prevention of the spill from reaching the plant drainage or storm-drain system. Because many of the gratings over storm and sanitary drains are cast iron, most of these covers are magnetic and designed to adhere to the drains, sealing them from the spill. In other cases, plants and industries have employed plain heavy duty covers and used sandbags to help seal and protect the drains.

3 Chemical Spills vs. Oil Spills

Chemical spills, unlike crude and other oil spills are generally confined to one product. While one cannot write a single chemical equation for an "oil" or "petroleum product", one can write a formula for most solvent or chemical spills.

The selection of spill control materials for spill prevention and containment needs to be based upon the chemical formulation of the spilled material. If the selection of containment materials is not suited to the material spilled, the spilled materials can easily dissolve the containment barriers or have energetic chemical reactions with the barrier materials. Consideration of the type of materials and their potential quantities is important in developing an effective spill control program.

4 Booming and Containment

Many of the compounds in crude oil float, creating a layer on the surface of water which can be as little as a few microns (creating a sheen), to millimeters, to several centimeters—the height of the top of the boom (5-10 cm). One of the ways to prevent the oil from spreading is to provide a physical barrier or oil boom. The boom itself is a plastic or rubber material not attacked by the oil[v]. The boom material may also contain a heavy cloth or plastic affixed to a flotation device, and it is weighted on the bottom so that it forms a vertical barrier to the spreading of an oil slick.

There are many types and kinds of oil booms. Some are weighted with chains for stability and others have internal weights incorporated into the boom material. The weight keeps the boom upright, forming a containment barrier. The flotation booms sizes range between 0.2m to 1.22 m in depth. Some booms are designed to be towed while others are designed to be stationary. The towed array booms are attached to top and bottom cables which hold the boom materials together both to assist in deployment and to provide anchorage or a method of towing. Some booms are metal and are fire resistant, used when burning off an oil slick is the preferable method of treatment.

The manufacturers of booming equipment each have their own designs: the US Minerals Management Service, the USEPA, and USCG and the Canadian Government have developed a manual on the effectiveness and types of oil booms available[vi]. The evaluation is over 20 years old, but is still relevant and a good information source.

The design of the boom and its freeboard (height above water), size, depth below water, wind and wave action can have a significant effect on the performance of the containment booming. Wave heights of 0.7 Meters or more, often generated by a 7-15 mile per hour wind, can cause booms to be ineffective in containment of floating oil. In harbors, wave heights are lower than in the open sea, and booming more effective. Booming is often placed around moored ships to contain oil spilled during refueling operations.

A spill control boom's performance is affected by wind and wave action and the design of the boom: the height and depth of the boom on the water, and the position of the floatation attachment. For booms with lower freeboard, "wash over" can be a significant problem. In general, booming with greater dimensions (1.25M vs. 0.31M total height) are more effective because of the projections both above and below the water.

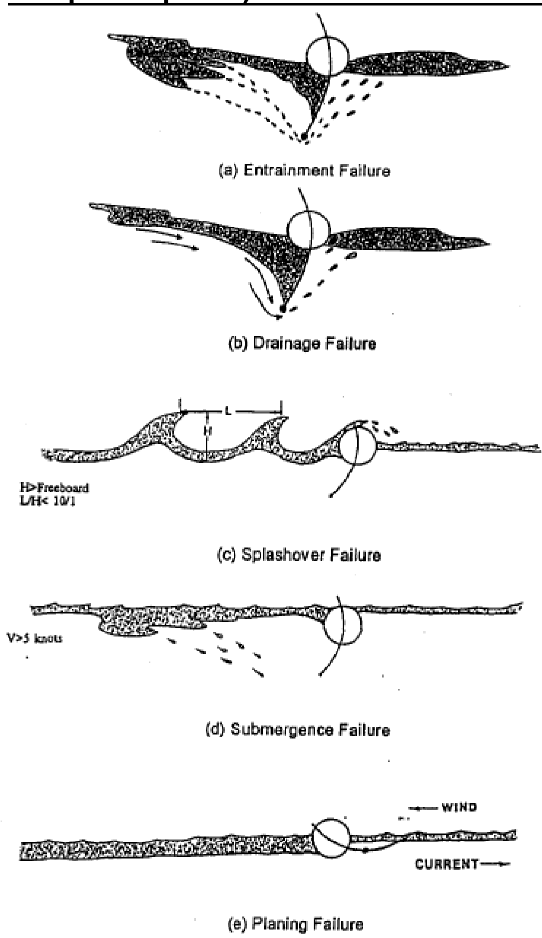
Some spill containment booms are designed for towed arrays—to be pulled behind a vessel to collect the oils. These booms are attached by a top and bottom cable linking each section of the boom to its neighbors: the boom is then deployed in a U configuration and pulled through the water much like a buoyant net or parachute. Towed arrays are often partially successful, especially in quiet open water but have challenges with stability in rougher water. The booms can not be towed at a speed of greater than 1-3 knots without significant losses through the boom.

Boom placement can be a huge issue in protection of an area. Booming should be deployed at an angle to the shoreline (lake, river, or ocean) in a chevron pattern, in layers, to direct the spill toward collection areas. Wind, wave, and currents along the shore and at shallow sea depths will affect the placement of the booming for effective spill recovery. The ultimate purpose of booming is never to prevent the chemical or oil from reaching the shoreline but to minimize it and recover or contain the spill and protect shoreline exposure as far as practical. Booms can not provide 100% protection from oil or chemical spills or leaks, but they can minimize the impact of those events.

Figure 3 is taken from the Booming Manual[vii] cited above, and it illustrates the five ways in which oil booms fail during use. Those methods are: entrainment failure; drainage failure, splash-over failure; submergence failure, and planning failure. Planning failure is one of the most difficult to compensate for because in open waters, currents and winds often shift, causing the boom to pass oils and other floating chemicals.

Effective boom placement is a combination of experience and science. In fast moving rivers, booms are primarily set in chevron style overlapping patters at an angle to the current. For fast waters, a chevron style deployment pattern is used in an effort to divert the spill to one specific location on the bank where it can be recovered more easily in a "quiet water" area created by the booming.

Figure 3: Types of oil boom failures: Taken from
<u>Oil Spill Response, Performance Review of Booms.</u>

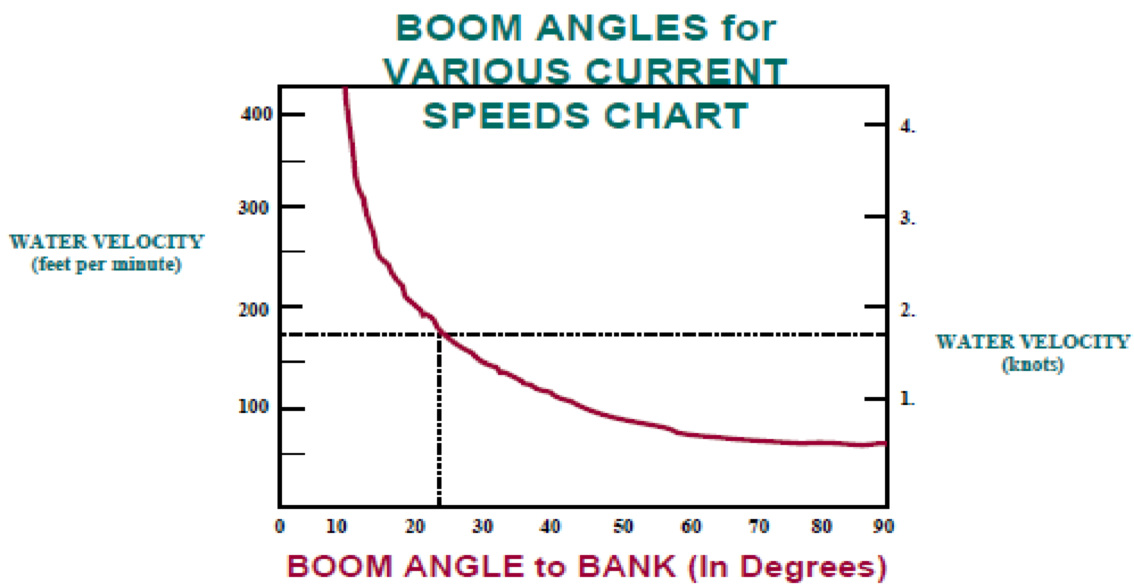


Booming which is used for protection of shoreline or structures, often requires a substantial "sea anchor" offshore to prevent movement and wash up upon the shore or river bank. Multiple heavy anchors are required for boom stability, depending upon the length of the containment. The shore protection booms are deployed far enough out from shore so that waves are not breaking over the boom.[viii]

Anchorage of the boom to the shore is also very important for protection of the shoreline. The shore boom is connected to the sea boom and has one end anchored, well above high tide, and beyond the point where minor rough weather will not dislodge the anchor. Many of the shore booms are partially buried for stability at the point of contact with the shore to provide additional anchorage for the boom.

The placement of a boom in a flowing river depends upon the geometry of the river channel and the velocity of the water. For very quiet rivers, the booming can be essentially perpendicular to the direction of the flow. The angle of placement increases with the speed of the current to a approximately 10^o to the normal direction of the current for faster moving waterways. Guidance on boom placement can be found in the documents referenced in Endnote VII and shown below.

Figure 4 Booming angles for various current speeds in flowing water.



Plot of the Maximum Angle for Boom Deployment at Increasing Current Velocities.

Source: Unique challenges of booming in fast flowing rivers – see endnote vii

In instances where the oil or chemical spilled is thicker, and flammable, the easiest method of cleanup is to set the layer on fire to destroy a significant amount of the floating material. This requires special “fire booms” able to withstand the heat while maintaining their shape and buoyancy. Fire booms are often deployed around a spill in the open ocean where the oil is thick enough to support combustion.

Spill control booms are imperfect instruments for containing oil and chemical slicks in open waters and wherever there is a combination of wind, wave, and current actions in open seas or near shorelines. Booms they are often the best tools we have available to contain and clean-up a spill.

5.Dispersants

On some occasions, where there is little danger of impacting shore lines, dispersants are used. The dispersants are organic detergent compounds which help break up the surface tension of the oil slick and cause it to emulsify and break down into smaller molecules which the indigenous bacteria can use as food.

The use of dispersants is often controversial because of their toxicity. Pre-deployment of dispersants, a number of factors should be considered, including: regulatory approval; effectiveness of the dispersant; toxicity and breakdown compounds of the dispersant on the aquatic environment including fish, birds, amphibians, and mammals; effectiveness of the dispersant on the spill over time; deployment method and time required for deployment; effectiveness of deployment methods; precision of deployment methods; available equipment and area to be covered; ambient conditions in the area of the spill; and personnel and their training for dispersant use.

6 Oil and Chemical Recovery and Treatment

The general chemical formula for bacteria is approximately 100-125: 20: 1 for Carbon Nitrogen and Phosphorous. For complete degradation Oxygen is also required: two molecules of Oxygen are required per molecule of Carbon in order to form CO2, the end product of aerobic decomposition. Oil is a carbon rich source, deficient in N and P. Dispersants help break down the oil but for complete bacterial action, Oxygen, some Phosphorous, and Nitrogen are required; and the use of dispersants often leads to oxygen depletion in the water. Dispersants can also be quite toxic to several forms of aquatic life. For example, 973,000 gallons of Corexit© was used in dispersing part of the Deepwater Horizon spill, and according to health reports, the dispersant compound has the potential for creating asthma-like symptoms in exposed humans and can damage gills of marine creatures [ix]. The aquatic effects of dispersants are often not fully described in the Material Safety Sheets.
Recovery of floating oil, even after it is contained is a messy operation. There are a number of floating devices which will enhance recovery of the floating oils. Some are wheels, brushes, or belts which have an affinity for the oils, and attract the oils to their surface. The belts, and brushes and wheels processed through a series of rollers or scrapers which either squeeze out the oil or scrape the belt surface to remove the oil. The oil is collected in a separate container. The concentration of oil in the collected material seldom exceeds 15%. Vacuum trucks and suction devices are often employed for collection of the oil, at a slightly lower oil to water (1%-2%) ratio. The temperature of the water and oil is always a factor, and thicker oil will not only be more difficult to recover, but the ratio of oil to water will be even lower.

Once recovered, if the viscosity is low enough, the oil can be processed through a coalescer to concentrate the oil. Otherwise, for heavier oils, an API separator is often used. An API separator is a long rectangular tank with baffles to prevent short circuiting. Typical retention times are 30-60 minutes, and the oil/water mix feeding the separator should not be fed by a centrifugal pump because of the emulsification factor associated with the pump impeller. Some coalescers do not have this problem because they use a fiber mat as the separation medium.
In one instance an oil collector employing a buoyant polyethylene rope was used for an oil collection device from a tank. Vegetable oils clung to the rope on one cool evening and increased the diameter of the rope from 1 cm to around 5 cm. At the 5 cm diameter, the rope

plus oils were too heavy for automated equipment to lift and run through compression rollers which would remove the oils. The oils congealed and behaved more like grease, clinging to everything and ultimately burning out the motor on the oil recovery device. This may not be an uncommon occurrence, and choice of the oil recovery system has to be made with respect to the properties of the oil to be recovered.

7 Beach and Bird Cleanup

Beach cleanup is perhaps the hardest to accomplish next to wetland cleanup. Oil gets into the interstitial spaces between the sand grains or it enters the pits and crevices in rocks where it is very difficult to remove. As discussed above, the environment of the affected area is often a factor because the oils and chemicals are sometimes viscous or congealed or in "tar balls". It is often impractical and extremely expensive, but effective beach cleanup may require removal of the contaminated sand and processing it through a sand washer with detergent and hot water to remove the oils. In beach restoration, the rocks may have to be washed it down with high pressure hoses and biodegradable detergents, and hot water as well, depending upon the nature of the oil and its viscosity. The cleanup videos from the Exxon Valdez illustrate this point[x].

Wetlands are natural biological factories which in time, if they survive the damage arising from the damage or toxicity of the oils or chemicals, can degrade the oil in a few months to a few years. Oil is often toxic to plant life, and exposure to large quantities of oil can effectively kill a wetland or at least damage it for several years until it has a chance to develop the enzymes required to metabolize the oil, and its heavier components.

Spills can contaminate animal life, particularly water birds, crustaceans, and fish. The shrimp harvest in Louisiana was highly contaminated by the Deepwater Horizons spill, and the oil rendered much of the seasonal catch inedible.[xi]. For waterfowl, the oil gets into the feathers and if it is not toxic, can impede their ability to float or fly. Oil can also interfere with the birds' food sources, and taint the aquatic plants and animals upon which they feed. Oil in a bird's digestive tract is harmful and can be fatal[xii].

Bird sanctuaries and wetlands should be protected at all times; given priority for protection in the event of a spill. In the US, and some other countries, it is illegal and dangerous to rescue or attempt to rescue waterfowl without a federal license and training. Bird rescue and cleanup has to be performed by licensed professionals who not only wash the oils off the birds, but who then reapply a different oil to the feathers of waterfowl so that they do not get waterlogged and drown.

8 Spills on Land: Contamination of Groundwater

Some of the most difficult and troublesome spills to clean up are spills on land. The lower the viscosity of the spilled material, the greater challenge it will be to clean it up, and the greater cost of the cleanup. For example: Bunker C or Number 6 Oil is viscous at around 200°F (93.3°C). Below that point it is semi-solid and solid. A spill of hot oil contacting the ground will solidify quickly and will penetrate the ground only a few centimeters. Cleanup is accomplished with a shovel and only a very small (<0.1) of the oil is mobile or soluble to be conveyed to the groundwater.

By comparison, gasoline, kerosene, and many refined oil fractions and lots of chemicals have much lower viscosities. They can and will enter the soil and make their way down to the groundwater. It has been estimated that for 100 units (either gallons or liters) of a refined petroleum product, such as No 2 Diesel Oil spilled on to a sandy soil or sandy loam, approximately 75% will remain above the groundwater, smeared into the intersticies of the soil particles. About 24% of the spill will be found floating on the surface of the groundwater in a lens shaped structure. The remaining 1% of the material will be dissolved in the water column, migrating with the groundwater.

The cost of the cleanup is in inverse proportion to the amount of material: If the cleanup of the material in the interstices costs 1 unit of cost, the cleanup cost of the floating material will cost approximately 10 times the interstitial cleanup cost, and the dissolved material may cost 100 times the cost of the interstitial cleanup cost[xiii]. This of course depends upon the viscosity of the material spilled, temperature, soil grain sizes, and other factors.

Remediation of the groundwater is generally out of scope of this article because of the complexities, and detail required for satisfactory explanation of the topic and techniques is too long for this article, and various treatises on the topic have been published in book form. However, the cleanup of the groundwater can not be accomplished until the surficial and other soils above the groundwater have been cleaned up. The general techniques for groundwater cleanup include 1) pumping and treatment of groundwater by extraction and treatment of the pumped groundwater to remove the contaminants; 2) vapor extraction- injection and/or withdrawal of the air above the groundwater to evaporate the contaminant materials in the soil interstices which may, depending upon the nature of the contaminant also remove materials from the water column; 3) groundwater vapor stripping by injection of air into the groundwater beneath the contaminant plume combined with vapor extraction of air above the groundwater; and 4) chemical and organic enhancement of the groundwater to encourage natural attenuation. All of these remedial techniques are expensive and require the installation of a number of exploration and production wells, and long-term monitoring.

In recent years, and because of the cost of remediation, many states are engaging in natural attenuation for the lighter petroleum fractions. This approach lets Mother Nature perform degradation of the contaminants through action of the natural bacteria in the soils.

Another technique suitable for shallower soils (less than 10 meters in depth) is specific types of phytoremediation. For shallow contamination, trees and certain plants will remove the contaminants and expire them through their leaves or treat them through their rhizomes. The process of natural attenuation is extremely slow, and for recalcitrant compounds, it can prove unsatisfactory[xiv]. The recalcitrant compounds described often are the phenol and asphaltene compounds and other high molecular weight and complex organic materials. The simpler compounds such as benzene, toluene, etc., are volatile and can often be Phyto remediated and bioremediated by natural means.

The best way of preventing groundwater and water contamination is not to allow it to occur in the first instance.

9 Other Solutions: Diking

Many companies in the petrochemical industries have recognized the potential damage from accidental spills of oil and chemicals. Many storage areas are protected with spill control diking—earthen berms or concrete walls, designed to contain the spill in the vicinity of the tank.

Occasionally, spill control diking is built without proper consideration of the permeability of the underlying soils. Some petroleum terminals built on sandy soils have the dikes surrounding the tanks built from natural materials -- porous natural sand. Any chemical or refined petroleum hitting the sand will permeate into the groundwater, where it is difficult and expensive to remove [xv].

A 1997 oil spill newsletter, was partially funded by the EPA, estimated that for every 100 gallons of oil spilled on to soils, between 70% and 73% would be trapped in the soil; 20% to25% would be floating on the groundwater, and 1% to 3% would be in a dissolved plume in the groundwater. If the cost of removing the gasoline from the soils is X per unit quantity removed, the cost of removing floating gasoline from the groundwater surface is somewhere between 5X and 10X; and the cost of removing dissolved gasoline from the groundwater is another multiple higher than the removal of floating gasoline. The cost is even higher if the groundwater is a drinking water aquifer. The residual contamination permitted in drinking water is extremely low.

Darcy's Law calculations can be used to estimate the permeability of the soils in the diked area. Calculation of the time required for observation and response and remedial activity with respect to the speed of a spill permeating into the soils, could provide guidance for determination of the adequacy of the dike permeability.

Endnotes

i Vanadium is particularly troublesome. While it is only 5-10 ppm by weight, it can reduce the efficiency of the hydrotreater in the refining process.

ii Viscosity is measured in centipoise and centistokes. Centistokes are the viscosity of the fluid divided by the density of the fluid, which for many petroleum products is about 0.85-0.9; centistoke velocity is about 15% (approximately) than the centipoise values.

iiiViscosity of water is approximately 1 centipoise. Crude oils have viscosities approaching 100-1000 cp at sea temperatures. see: http://petrowiki.org/File:Vol1_Page_288_Image_0001.png

iv http://www.cstsales.com/viscosity.html

v The exception is fire booms which are generally made from metal and are designed to withstand the high temperatures which are generated when an oil slick is deliberately set on fire.

vi Oil Spill Response, Performance Review of Booms, by Robert Schulze. Publication is available from:

https://www.bsee.gov/sites/bsee.gov/files/osrr-oil-spill-response-research//330aa.pdf

vii Other sources of information include:
https://www.mass.gov/files/documents/2016/08/on/basic-booming-techniques.pdf and
http://www.itopf.com/fileadmin/data/Documents/TIPS%20TAPS/TIP3UseofBoomsinOilPollutionResponse.pdf
https://archive.epa.gov/emergencies/content/fss/web/pdf/c_oskins2_04.pdf

viii https://www.youtube.com/watch?v=LrOYoE-Hrp4

ix UAB Medical Program, as reported in PLOS One in April 2, 2015, and summarized on the UAB Website:
http://www.uab.edu/news/research/item/5923-uab-study-suggests-oil-dispersant-used-in-gulf-oil-spill-causes-lung-and-gill-injuries-to-humans-and-aquatic-animals-also-identifies-protective-enzyme

x https://www.youtube.com/watch?v=hD7zq94Twdg, and https://www.youtube.com/watch?v=YkzB1ZYcTwM

xi One estimate of the losses is 94 Million Dollars for Louisiana alone:
http://www.nola.com/environment/index.ssf/2016/06/bp_spill_cost_gulf_fishing_ind.html

xii For more information see International Bird Rescue Service:
https://www.bird-rescue.org/our-work/research-and-education/how-oil-affects-birds.aspx

xiii Remediation Manual for Contaminated Sites Oct, 2011 by David L Russell, PE., CRC Press, available in e-pub format from Amazon and others.

xiv Dr. Nelson Mamiroli, University of Parma, Italy, has referred to phytoremediation as “Diluting the contamiants in time.”

xv A spill in El Khafji, Saudi Arabia, (Summer, 2014), of approximately 55,000 barrels of crude oil was released into a sandy diked area. Approximately 50,000 barrels of oil were recovered from the spill. The balance was in the ground and floating on the groundwater.