

**Temporal Constraints on Free Phase Floating Petroleum Product
Rebound in the Upper Glacial Aquifer, Long Island New York**

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Abstract

The authors have had past experience with sites in which free-phase petroleum has reappeared on the water table after significant periods of time (years). In order to better understand this phenomena we have compiled data on five sites in which free-phase petroleum has reappeared after a period of years. In all five cases the reoccurrence of free-phase petroleum was preceded by a drop in the water table elevation. The time lag between the drop in water table elevation and the appearance of free-phase petroleum ranged from 0.125 to 1.08 years. This time lag may vary at different sites depending on site specific parameters such as soil permeability, the residual saturation capacity of the soils, the organic carbon partition coefficient and the degree of saturation of the soils. For example the site with the lowest hydraulic conductivity was also the site with the fastest rebound following the drop in the water table. This was due to the degree of soil saturation with respect to petroleum. This paper provides temporal and hydrogeologic constraints on the reoccurrence of free-phase petroleum. In addition, we review several remedial alternatives that address petroleum soil contamination in combination with product recovery.

Introduction

In recent years many studies have concentrated on petroleum contamination of soils and migration of said petroleum through the unsaturated zone (Bradner and Slotboom, 1975; Larson et al., 1980). However, although conceptually understood, the temporal aspects of free-phase petroleum rebound after apparent remediation are not well understood. After free-phase petroleum is recovered from the water table it is likely that the remediation system may be shut down after no petroleum product has been detected for a period of several months. Often, after a period of years, the petroleum product may reappear as free-phase petroleum on the capillary fringe or water table. This was demonstrated by the authors in five case studies in which free-phase petroleum product occurred on the water table. Remediation systems had been installed to recover the free-phase petroleum product. In the case of gasoline, an air stripper tower and a pump and treat system were installed, where as, for Number 2 fuel oil, an oil water separator with final polish by carbon canisters was employed. After the product had ceased to occur for a period of several months to years the systems were shut down. Monitoring of the sites continued on a monthly basis. In all of these case studies the authors have demonstrated that free-phase petroleum product (both gasoline and fuel oil) have increased or completely rebounded on the water table from 0.125-1.08 years following significant drops in the water table elevations. The authors feel that the key parameter allowing for the reoccurrence of free-phase product is water table fluctuation before soils have been completely remediated.

Five case studies are described by the authors to establish the temporal aspects of the rebound of hydrocarbons on the water table after a drop in the elevation of the water table. The case study areas are located in Nassau and Suffolk Counties in New York State. Furthermore, all studies involved gasoline, jet fuel or No. 2 fuel oil. This paper will demonstrate the time it takes for product to rebound in light of the subsurface hydrogeologic conditions and water table fluctuations. In addition, a number of soil remediation techniques in conjunction with free-product recovery will be discussed.

Geology of Long Island

Long Island is underlain by Precambrian basement rocks including gneiss, schist, limestone, and granodiorite which outcrops in a few localities on the northwestern edge of Queens County. From this point the bedrock dips to the southeast. Unconformably overlying the bedrock is an unconsolidated wedge of sediments dating from the Cretaceous, Pleistocene and recent. The sediments obtain a

thickness of greater than 1,000 feet in southeastern Long Island. These sediments comprise several important aquifers serving as the sole source aquifers for Long Island.

The stratigraphic sequence of the unconsolidated material is as follows:

The Raritan Formation is the deepest unit and rests directly on the bedrock. The formation is comprised of a sand member (Lloyd aquifer) and a clay member (Raritan Clay). The clay member acts as an aquitard confining the lower Lloyd aquifer between the clay and the underlying bedrock. The Lloyd sand extends southeastward from Flushing Bay to the Atlantic Ocean. Thickness of the sand member increases to the southeast and its surface ranges in depth from 200-800 feet below sea level (from northwest to southeast).

Directly overlying the Raritan Formation is the Magothy Formation. The Magothy is comprised of interbedded clays, sands and gravel. The upper surface of the formation is irregular and in places is an erosional unconformity. In several areas this formation is absent from the stratigraphic column reflecting the high rates of erosion which preceded deposition on the Pleistocene units.

The Magothy Formation is also a prolific aquifer. Coarser sand and gravel layers, which are the most productive are commonly found in the lower 50-200 feet of the aquifer. Both confined and unconfined conditions exist in the aquifer due to the presence of more impermeable clay and silt lenses. In Queens a second aquifer exists as a submember of the Magothy formation. Several buried valleys in the eroded surface of the Magothy Formation are filled with coarse sand and gravel. These materials are known as the Jameco Gravel and Monmouth Sands. The greatest extent of these sands is found in a deep buried valley extending from Flushing Meadow to Kennedy Airport. The valley is believed to be an ancient channel of the Hudson river.

Upper Pleistocene age glacial materials overlie the majority of Long Island. This material rests unconformably above the underlying strata. Three types of glacial material are present: Terminal and Recessional Moraines, broad outwash plains, and glacial till deposits.

The surface areas of Long Island, not covered by glacial material, are covered with shore and salt marsh deposits (recent) or filled material.

Results

Below we will present five case studies in which free-phase petroleum has reappeared after years of absence. The hydrogeologic specifics are summarized in table 1.

Table 1. Site specific hydrogeologic parameters.

	Petroleum Type	Density of Bulk Product	Soil Type	K cm/sec	Hydraulic Gradient ft/ft	Time to reoccurrence
Case 1	No. 2 Fuel Oil	0.82-0.86	Medium sands	$\sim 10^{-2}$.003	-
Case 2	No. 2 Fuel Oil	0.82-0.86	Silty Clay Peat	$\sim 10^{-5}$.013	0.125
Case 3	Jet Fuel	0.77-0.83	Outwash Deposits	$\sim 10^{-2}$.046	1.08
Case 4	Gasoline	0.72-0.78	Glacial Till	$\sim 10^{-3}$.023	0.43
Case 5	No. 2 Fuel Oil	0.82-0.86	Outwash Deposits	$\sim 10^{-2}$	-	-

Case Study I

In 1984, an underground storage tank leaked approximately 5,000 gallons of Number 2 fuel oil. Following the spill, a free-phase petroleum product recovery system was installed, and monitoring wells were sampled and analyzed on a scheduled basis. Following the disappearance of free-phase petroleum in June 1991, the remediation system was shut down.

The site is underlain by approximately 1,100 feet of unconsolidated coastal plain sediments of Cretaceous, Tertiary and Quaternary age. The uppermost unconsolidated unit, which is Pleistocene in

age, consists primarily of glaciofluvial sediments derived from the melt-water of the retreating glaciers. These deposits are generally stratified, moderate to well-sorted sands and gravels.

Groundwater on site occurs in the basal part of the Upper Glacial Aquifer and the Magothy Aquifer. The subsurface soil consists primarily of glaciofluvial deposits, medium sands with small percentages of pebbles. The hydraulic conductivity on site is in the approximately 40 ft/day. In 1991 the water table was approximately 30-31 feet below grade. Presently, the water table is at a depth of 39-40 feet below grade at an elevation of approximately 70 feet above mean sea level with a hydraulic gradient of .003 ft/ft.

In 1994, after a drop in groundwater elevations (figure 1), free-phase petroleum reappeared on the site. On May 10, 1994 soils were sampled using the split spoon method. Results of field screening, using a portable Gas Chromatograph, indicated that the elevated BTEX concentrations were found in soils from the 28 to 40 foot intervals. Subsequent laboratory analyses confirmed that soils at these depths contained the greatest concentrations of Volatile Organic Compounds.

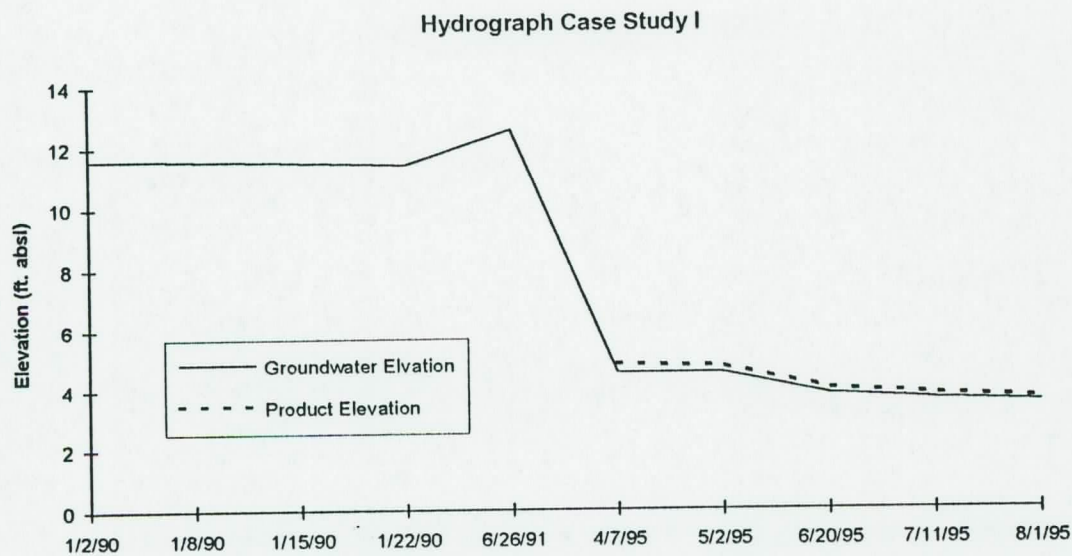


Figure 1. Hydrograph of case history I showing the reoccurrence of free-phase petroleum following a drop in the water table of approximately 8 feet..

Case Study II

In 1987, free-phase petroleum was detected at an oil terminal in Nassau County New York. This site was severely contaminated with free-phase petroleum with thicknesses as much as 8.58 feet in some wells. Between 1987 and 1991 a remediation system consisting of two (2) product only ejectors with a 7.5 hp air compressor was employed to eliminate free-phase petroleum. Product was stored in a 1000 gallon above ground storage tank. Since remediation began, 1,339.5 gallons of product have been recovered.

The site is located on the Queens-Nassau County border in close proximity to a salt-water bay. Beneath the site the Magothy Aquifer occurs at approximately 200 feet below sea level. The strata above the Magothy aquifer are primarily composed of glaciofluvial sands and recent deposits. The near subsurface geology is composed of silty tidal flat deposits, hence the permeability and hydraulic conductivity on site are moderate to low, 0.089 ft/day. Groundwater occurs at depths as shallow as 2 feet below grade.

A hydrograph (figure 2) was prepared for monitoring well which currently contains 1.32 feet of floating-fuel oil product. The hydrograph reveals that following clean-up of free-phase floating product the groundwater elevations dropped 3-4 feet above sea level to 1.5-2.5 feet above sea level. Approximately 0.125 years after this drop in the water table elevations, floating product reappeared on the water table. As the water table dropped a zone of residual contamination was exposed. We believe

that the lack of a time lag between the drop in the water table and the reoccurrence of free-phase petroleum reflects the saturated nature of the soils on site with respect to fuel oil.

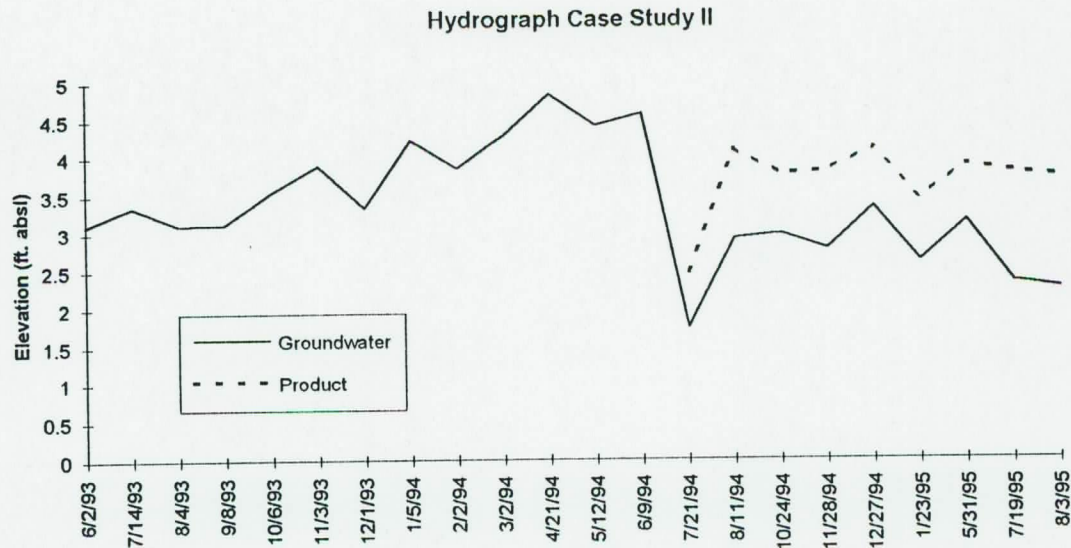


Figure 2. A hydrograph of case history II showing the reoccurrence of free-phase product one month after a drop in the water table elevation.

Case Study III

The Site is located in Nassau County on glacial outwash plain deposits consisting primarily of sands and gravels. The Magothy Aquifer occurs, approximately 25 feet below sea level. The hydraulic conductivity on site is approximately 28.35 ft/day. Groundwater from the upper glacial aquifer occurs at depths of 23 to 28 feet below grade with a hydraulic gradient of 0.46.

Case study three describes the reoccurrence of free-phase petroleum (Jet Fuel density = 0.77-0.83 grams/liter) at an airport in Nassau County. We had been monitoring the site since 1993. In 1993 we began a subsurface investigation to determine the extent of groundwater and soil contamination. During the course of the investigation it was found that soils showed high concentrations of petroleum hydrocarbons at depths of 18-22 feet. Groundwater at this time occurred at depths of 20-23 feet.

A hydrograph (figure 3) was prepared for a monitoring well currently containing free-phase petroleum. Inspection of the hydrograph reveals that prior to 1995 the water table was found at depths less than 20-23 feet. During this time period no free-phase petroleum was found on the site but appeared as residuum in the soils. However, in June of 1995 the groundwater table dropped to depths of greater than 25 feet. At this time free-phase petroleum was first detected on site. As the water table has continued to drop the thickness of free-phase petroleum has increased. The product reappeared 0.75 years after the water table dropped below 45.5 feet above sea level.

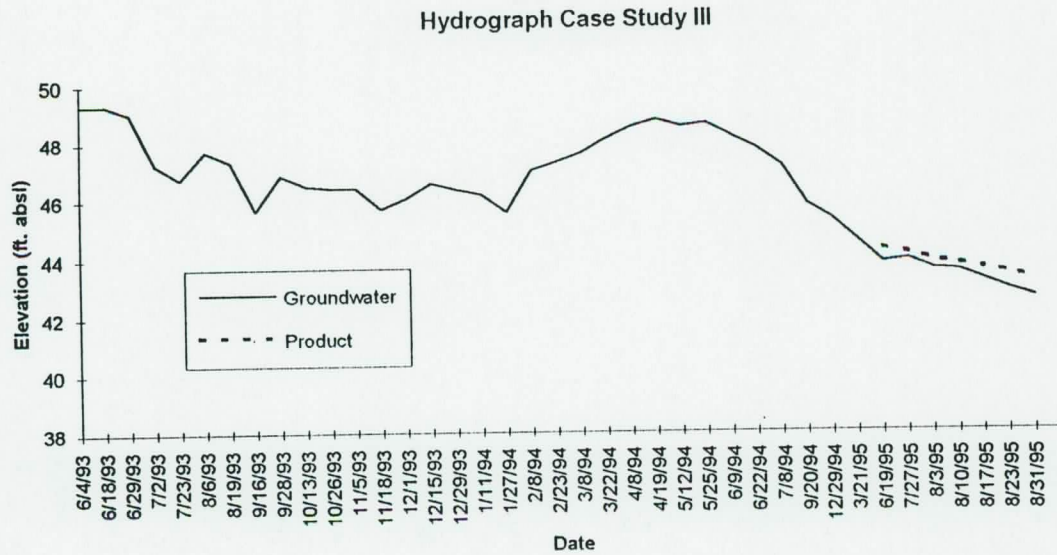


Figure 3. Hydrograph of case history III showing the reoccurrence of free-phase product 0.75 years after a significant drop in the water table.

Case Study IV

In early 1984, a drinking well at the private residence located south of the site detected an odor of petroleum hydrocarbons in their tap water. The NYSDEC ordered the residence to connect to the Suffolk Water District System and abandon their private well. The NYSDEC subsequently investigated the site, installing a total of nineteen (19) monitoring wells and a recovery well.

Remediation began following the detection of free phase petroleum (gasoline) in some of the monitoring wells. F&N installed a recovery system consisting of a floating filter scavenger with a water table depression pump, a 4" flow meter, an air stripper tower, and a 1,000 gallon product recovery tank. Following the decrease in free phase petroleum, the product recovery system was shut down in November of 1992. After a period of 0.43 years following a drop in the water table elevation, free phase petroleum reappeared in December of 1994.

On August 23rd, 1994, one soil boring was installed in the vicinity of the tank area in order to determine the extent of soil contamination of site. Continuous split spoon sampling was performed to approximately ten feet (10), below the water table. All the soil samples were field screened and two soil samples were analyzed by EPA method 602 for BTEX. These samples showed a zone of soil contamination above the water table.

In order to determine any correlation's between the reappearance of free-phase petroleum and fluctuations in groundwater elevations a hydrograph was prepared (figure 4). Product was first noted in December 1994 when the water table dropped to seventy three feet below sea level. Prior to this time, groundwater elevations were approximately three feet above the present levels. When groundwater elevations dropped in November 1994 free-phase petroleum was continually detected in monitoring wells from the site.

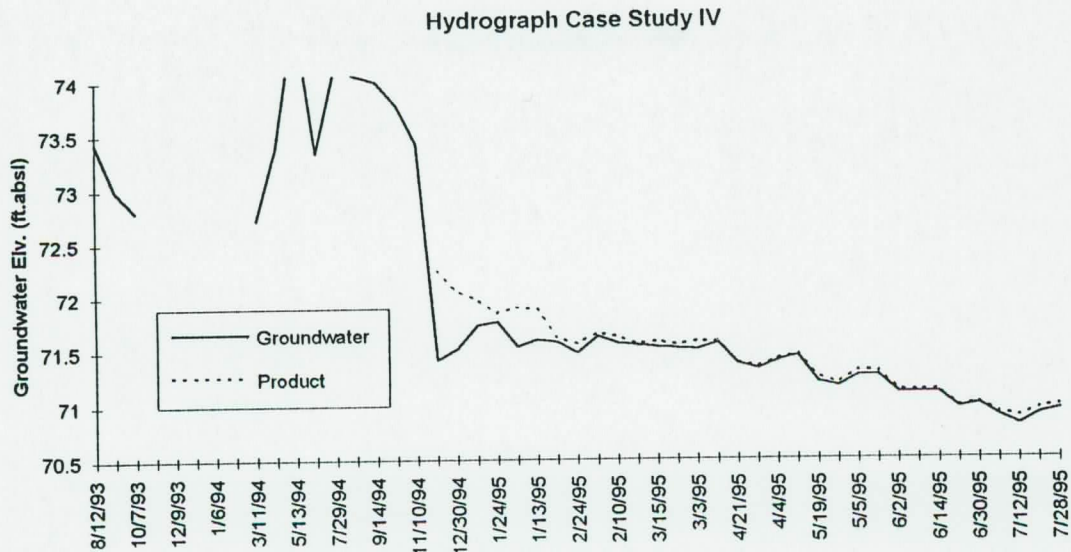
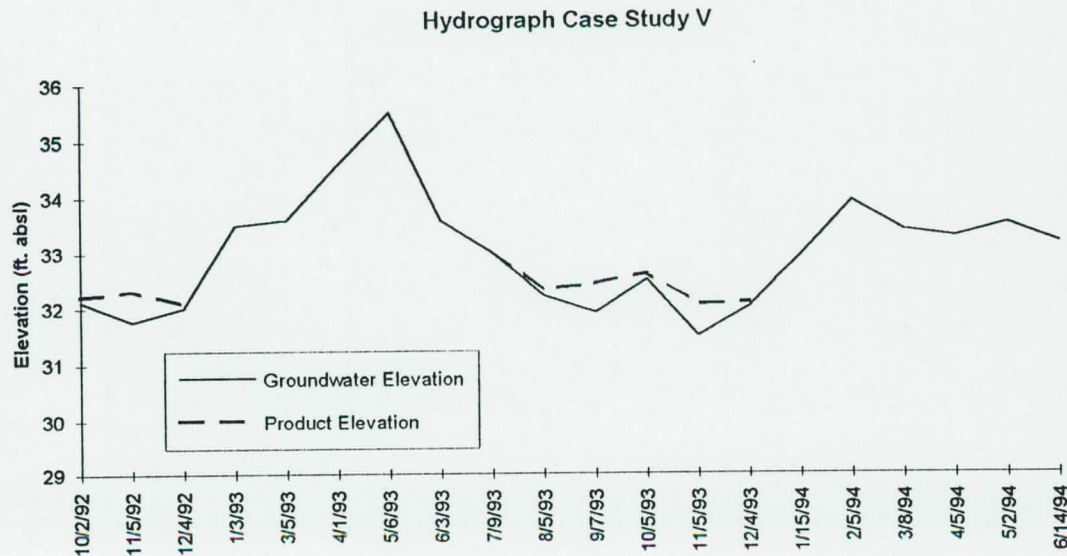


Figure 4. Hydrograph for case study IV showing the reoccurrence of free-phase product 0.43 years after a drop in the water table elevation

Case Study V.

Case study V involves a private residence located in Babylon N.Y. Groundwater in this region occurs in the Upper Glacial Aquifer. The Magothy Aquifer occurs at approximately 25-50 feet below sea level. On January 27, 1992, number 2 home heating fuel oil was spilled on well drained, medium-textured and moderately coarse textured soils of outwash plain affinity. These soils exhibit moderate to high permeability, allowing for optimum migration rates. Beneath the site, groundwater occurs at depths of approximately twelve (12) feet, providing a natural barrier for vertical migration of the home heating oil. The aquifer is also characterized by fluctuations in groundwater elevation (figure 5) due to seasonal changes in precipitation amounts.



In June, 1994, monitoring of the site was terminated due to the absence of free-phase petroleum for six consecutive months. Following continued complaints by the home owners a sample was taken

from well #3 on January 18, 1996. The sample was found to contain a film of free-phase floating product. This followed a drop in the water table during the summer and fall of 1995 due to drought conditions on Long Island. Examination of hydrograph (figure 5) reveals that when there was a period of time between December 1992 and July, 1993 in which no free-phase petroleum occurred. Following a drop in the water table in May, 1993, free-phase product once reappeared in July, 1993. As the water table rose in December 1993, free-phase petroleum was left as residuum in the soils.

Discussion

The five case studies presented above indicate that free-phase petroleum may return to the water table even after recovery of product from the groundwater. The authors believe that this is due to the presence of free-phase petroleum as residual contamination beneath the water table. If the amount of petroleum spilled exceeds the residual saturation capacity for a soil then the oil will continue to migrate vertically until it intersects the capillary fringe and the saturated zone (Dragun, 1988; Bossert and Bartha, 1984). When the hydrocarbons reach the saturated zone they are unable to continue to migrate vertically due to their immiscibility with water and their lower specific gravity. Therefore, the hydrocarbons spread laterally in the upper portion of the upper capillary fringe (Dragun, 1988; Farmer, 1983; Dietz, 1970). As the water table fluctuates the depth of the residual saturation zone, relative to the water table varies. When the water table rises the zone of residual saturation may lie below the water table, as the water table drops the zone of residual saturation will be exposed in the vadose zone. Once exposed, the residual product in the soils may be liberated due to gravitational forces and viscous displacement by percolating water (Farmer, 1983). In cases where we were able to apply time limits to the reappearance, the time varied between 0.125 to 1.08 years following the initial drops in the water table.

The reasons why the product remains after years of product recovery operations are not straightforward but involve the complex interactions of both physical and chemical properties of the petroleum and aquifer. Several factors controlling the retention of residual product in the aquifer are: adsorption of hydrocarbon molecules onto soil particles, viscosity and wetting angle of petroleum, the surface area of the soil particles, the water free pore space, the amount of downward percolating water and the velocity of the groundwater flow (Dragun, 1988). Capillary forces act to retain petroleum in the formation and resist mobilization into the aquifer. These forces in combination with adsorption act to keep the petroleum as a residual phase in the formation. In addition, the physical characteristics of the aquifer affect the amount of petroleum that can enter the formation as residual. In fine grained aquifers there is greater surface area on soil particles in which petroleum can collect due to adsorptive and capillary forces. In Case study II, the soils consisted of low conductivity silty peats. Thus there was a great surface area for adsorption. Therefore large amounts of residual product were able to be stored in the formation due to adsorption and capillary action.

Another physical action acting to retain the residual product over the years may be the low velocity of ground water in a region. Viscous forces act to force the hydrocarbons out of residual phase in the soils. If groundwater is flowing at high rates there may be enough viscous force to overcome the interfacial tensions between the petroleum and soil particles. In all of the above sites the hydraulic gradient was low. Thus the velocity of the groundwater flow was likely low resulting in decreased viscous force to remove the residual phase hydrocarbons. After these hydrocarbons were exposed in the vadose zone due to water table fluctuations, percolating water slowly displaced the residual phase from the pore spaces resulting in free-phase petroleum on the water table.

The five case studies presented above have shown that the disappearance of free-phase petroleum does not necessarily signify the site is remediated. In fact, all too often, free-phase petroleum returns to the water table following drops in water table elevations. This suggests that standard product recovery systems, in and of themselves, are not sufficient to bring a site to closure. Thus, it is important to consider further remedial solutions to incorporate with a standard product recovery system. These solutions should address the soil contamination both above and below the water table.

Several methods are available to remediate petroleum contaminated soils. The best method may be site specific and depend on the site hydrogeology as well as cost benefit analyses. Below, three methods are described that can be used in conjunction with a product recovery system:

In situ soil flushing is a process in which contaminants are washed from the soil by water or water plus a surfactant (detergent, or other solvent). Soil washing without the use of surfactants results in residual oil as various size ganglia (Larson et al., 1980).

Groundwater recovery systems are essentially soil flushing operations, although they are mainly intended to be containment systems. If in situ soil flushing is to be successful, the soil must be permeable to liquid flow (sandy soils). Conventional water flushing is practical for highly water soluble contaminants. For contaminants with lower solubilities (nearly all petroleum hydrocarbons) surfactant or solvents will be required. For highly contaminated soils (those which have free phase contaminant between interstices of the soil particles) surfactants can reduce contamination by at least two mechanisms.

- Reduction of free-phase contamination by immiscible displacement due to a lowering of the interfacial tensions
- Increasing viscous forces of displacing fluid
- Further reductions of free-phase and sorbed contaminant by solubilization (Martel and Gelinas, 1996).

With in situ flushing you have little control over the flushing fluid's flow path relative to the location of contaminants. Except for very sandy soils, it will be difficult to achieve uniform cleaning.

In situ bioventing is essentially a refinement of soil venting, but with bioventing the rate of movement of air through the aquifer is adjusted to the rate of microbial respiration so that emissions are kept to a minimum while oxygen is added to optimize microbial degradation (Thornton and Wootan, 1982; Crow et al., 1987). The purpose of moving air through the subsurface is to remove volatile petroleum contamination and deliver oxygen to the indigenous micro-organisms to promote natural biodegradation (Salanitro et al., 1989).

In-situ biodegradation consists of molecular breakdown of organic constituents via microbial degradation. Soil micro-organisms, principally bacteria, actinomycetes and fungi are the most significant group of organisms involved in biodegradation (USEPA, 1984). Environmental conditions are optimized by providing an oxygen source, nutrients and moisture (water) to enhance microbial activity. The feasibility of in-situ biodegradation is determined by the biodegradability of the organic constituents, soil characteristics which affect microbial activity, and the hydrogeology of the site. In-situ treatment is primarily effective for soil below the water table and groundwater. Treatment is accomplished by installation of a shallow infiltration system. Water, nutrients and an oxygen source percolate into the soil, enhancing microbial activity. A closed loop system is generally utilized, in which groundwater is pumped downgradient from the infiltration zone.

Conclusions

Based on the five case studies presented above as well as on the hydrographs produced for the subject site it is evident that the return of free phase petroleum is heavily influenced by fluctuations in the water table exposing contaminated soils in the vadose zone. Following the exposure of the soils floating product reappeared on the water table from 0.125-1.08 years, depending on site specific hydrogeologic conditions and the degree of soil saturation. When the water table dropped, free-phase product adsorbed on the soils was able to migrate vertically as water percolating through the soils displaced the petroleum from pore spaces. The importance of water table fluctuations on the rebound of free phase floating petroleum must be taken into account before a site is classified as closed or before a buyer purchases contaminated property. In order to avoid the reoccurrence of free-phase petroleum on the water table the soil contamination must be addressed. Viable means of remediating the petroleum contaminated soils include combinations of conventional pump and treat technologies, air sparging, soil vapor extraction, soil flushing, bioventing and in-situ bioremediation. Of these methods in-situ bioremediation shows the most promise for a wide variety of soil types.

References

- Bossert, I., and Bartha, R., 1984, The Fate of Petroleum in Soil Ecosystems. In Atlas R.M. (ed.). Petroleum Microbiology. New York: Macmillan Co.
- Bradner, C.F. and Slotboom, R.A., 1975, Vertical Immiscible Displacements in a Non-homogeneous Flow Cell. *The Journal of Canadian Petroleum Technology*. v. 14, n. 1., p. 27-33.
- Crow, W.L., Anderson, E.P., and Minugh, M.C., 1987, Subsurface Venting of Vapors emanating from Hydrocarbon Product on Ground Water. *Ground Water Monitoring Review*. v. 7, n. 1, p. 51-57.
- Dietz, D.N., 1970, Pollution of Permeable Strata by Oil Components, In Hepple, p. (ed.). *Water Pollution by Oil*. New York: Elsevier Publishing Co. and the Institute of Petroleum.
- Dragun, J., 1988, *The Soil Chemistry of Hazardous Materials*, The Hazardous Materials Control Research Institute, Silver Spring, MD
- Farmer, V.E. , 1983, Behavior of Petroleum Contaminants in an Underground Environment, In: *Proceedings of a Seminar on Groundwater and Petroleum Hydrocarbons*, June 26-28, 1983 Toronto, Canada: Petroleum Association for Conservation of the Canadian Environment.
- Larson, R.G., Scriven, L.E., and Davis, T.H., 1980, Percolation Theory of Two Phase Flow in Porous Media. *Chemical Engineering Science*, n 36 p. 57-73.
- Martel, R. and Gelina, P.J., 1996, Surfactant Solutions Developed for NAPL Recovery in Contaminated Aquifers. *Groundwater*, v. 34, n. 1, p. 143-154.
- Morrow, N.R., 1979, Interplay of Capillary, Viscous , and Buoyancy Forces in the Mobilization of Residual Oil. *Journal of Canadian Petroleum Technology* v. 18, p. 35-46.
- Salanitro, J.P., Wester, M.M., and Kembrowski, 1989, Biodegradation of Aromatic Hydrocarbons in Unsaturated Soil Microcosms. *Fifth national Conference on Petroleum Contaminated Soils*, University of Massachusetts Amherst, September 25-28.
- Thornton, J.S. and Wootan, Jr., W.L., 1982, Venting for the Removal of Hydrocarbon Vapors from Gasoline Contaminated Soils. *Journal of Environmental Science Health*. v. A17, n. 1, p. 31-44.