CHEMICAL ENGINEERING TRANSACTIONS
VOL. 28, 2012
Guest Editor: Carlo Merli

ISBN 978-88-95608-19-8; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1228003

Tidal Effect on LNAPL Mobility

Jean-Pierre Davit*[a], Sylvain Hains[b], Christophe André[c]

[a]Golder Associates Srl, via Banfo 43, 10155 Torino, Italy
[b]Golder Associates Ltd, 1170, boul. Lebourgneuf, Québec City, G2K 2E3, QC Canada
[c]Golder Associates Sarl, 31, rue Gorge de Loup, 69009 LYON
jpdavit@golder.com

The tidal influence on LNAPL movement is a subject poorly studied with limited literature available. Tidal fluctuations along shorelines create a unique condition where the migration of LNAPLs is buffered and often mitigated from discharging into an open water body.
A site investigation has been conducted in an area with presence of LNAPL located close to a major tidal river. The objective of the study was to assess the influence of the tide upon the distribution and mobility of a separated LNAPL body migrating toward the river. The Investigation area is strongly tidal-influenced and in a continuous transient state, and therefore the vertical equilibrium is never reached.
Baildown tests were performed at high and low tide in wells were LNAPL was present for assessing the physical characteristics of the LNAPL body. The baildown tests showed in general a low to very low recovery, generally not very affected by tidal fluctuation, since the recovery time is in general much longer than the tidal cycle.
Tidal influence appears to have a limited impact on measured NAPL thickness in the wells over time, but affects strongly the gradients, increasing locally the potential for NAPL mobility. The LNAPL body appears to be slowly migrating towards the river.

1. Introduction

A Light Non-Aqueous Phase Liquid (LNAPL) mobility and recoverability assessment was conducted at a former refinery. The investigation area is located along a main river under strong tidal influence from the nearby ocean. The existing well network at the Investigation area was deemed insufficient to assess the potential for LNAPL migration in the tidally influenced aquifer of the Site. Furthermore, the heterogeneous nature of the industrial fill in which the LNAPL is present influences his distribution and potential for migration as a separated phase by its own gradient, or as leachate by infiltration (seepage water) or tidal water entering the soil mass.
The tidal influence on LNAPL movement is a subject poorly studied with limited literature available.
The oscillations in groundwater along a shoreline produce a natural buffer zone that inhibits LNAPL migration toward the open water body. This buffer zone results primarily from the large smear zone that is produced due to the increased fluctuations in groundwater closer to the shore. As an oil plume migrates toward the shore, it will ultimately intersect the zone of tidally induced groundwater fluctuation. In this zone, any mobile LNAPL will become trapped as a residual as the oil plume is smeared vertically within the aquifer. The potential for vertical smearing increases toward the shoreline as the magnitude of the fluctuations increases (API, 2004).
In addition, the regular fluctuations in the water table acts to produce "snap-off", which breaks up the plume into isolated droplets within the soil pore network. In particular, because the groundwater fluctuations occur daily and consistently, it becomes difficult for the oil to coalesce into a consistent

Please cite this article as: Davit J.P., Hains S. and Andre C., 2012, Tidal effect on lnapl mobility, Chemical Engineering Transactions, 28, 13-18 DOI: 10.3303/CET1228003

plume of any significant thickness. Because the oil transmissivity decreases within the tidally influenced smear zone, the rate of migration of any potential mobile oil decreases as well. Hence, the tidally influenced smear zone is an effective barrier inhibiting oil migration (API, 2004).
It is important to mention however that tidal fluctuation will result in an increase of dissolved contamination, since product is continually being trapped and released with the water table changes, new LNAPL surfaces in contact with water increase and facilitate mass transfer from the LNAPL phase to the aqueous phase. As a result, groundwater concentrations commonly will be higher in areas of large water table fluctuations (API, 2004).
The literature reported above does not investigate the effect of the inversion of the groundwater gradient associated with saturation and desaturation effect on the LNAPL. In general, seasonal groundwater level fluctuations do not significantly alter the groundwater gradient, resulting in a vertical displacement with a groundwater table kept almost parallel to its original location. Tidal fluctuation significantly alter the hydraulic gradient in the soils over time cycles which are extremely short with respect of the groundwater movement time scale.

2. Objectives

The objective of the works was to carry out a characterization study capable of providing information to:
- Assess the LNAPL plume mobility and potential for migration into the river;
- Assess the potential transfer of hydrocarbon impact to the river via seepage water.

3. Approach

In order to conceptualize the Site conditions and delineate an approach for collecting the information needed for the study, a “transect approach” was selected. It was decided to gather information along lines of monitoring wells (“transects”) either perpendicular or parallel to the river as follows:
- 5 transects perpendicular to the river and to the tide, and thus parallel to the expected groundwater and potential LNAPL flow direction. The aim of these transects was to observe the variation of the tide movement inside the impacted area and the influence of the tide on the measured LNAPL thickness. 4 of the transects were selected within the recognized area of separated LNAPL, and one within impacted fill material with potential separated LNAPL sources.
- 1 transect parallel to the river and to the tide, but perpendicular to the expected groundwater and potential LNAPL flow direction.

4. Summary of field activities

Golder has carried out the following investigation activities at the site:
- Excavations of three 5 m deep trenches;
- Drilling and installation of nineteen 7 m deep groundwater monitoring wells. Soil samples have been collected every meter for chemical analysis;
- Scarification of a small cliff located on the northern beach at five locations along the river board;
- Repeated measurements at different tidal cycles of LNAPL thickness in selected existing and in new groundwater monitoring wells;
- Monitoring of groundwater and piezometric levels with pressure loggers;
- Slug testing in monitoring wells without measured separated LNAPL, in order to evaluate the hydraulic conductivity of the saturated soils;
- Repeated baildown testing to evaluate LNAPL recoverability at different tidal cycles in several wells.

5. Interpretation of the site investigation data

5.1 Investigations Area Geology

Golder assessed the Site geology to consist of a series of locally sub-horizontal lithological units. The lithological series, from top to bottom, can be summarised as follows:
- Topsoil;

- Fill material varying in thickness from 0m to over 4 m, made of reworked natural material and heterogeneous demolition material and operational fill materials, including hydrocarbons and tars;
- Recent alluvial deposits of fine sand and silt, with occasional lenses of coarser material of limited lateral extent. The majority of the soil samples can be classified as sandy silt or silt loam.
- Deeper quaternary alluvial deposits consisting of sand and gravel; and
- Chalk, comprising an upper highly weathered zone immediately below the Quaternary sands and gravels, becoming more competent with depth.

5.2 Investigations Area Hydrogeology

The groundwater heads across the Site are influenced by tidal variations in the River, with the magnitude of influence generally decreasing with distance from the river. The River is strongly tidal, with variations of more than 4 m between the maximum high tide and minimum low tide.

In the investigation area, variation of the piezometric level in the groundwater monitoring wells, is ranging between 0.03 m and 2.58 m below ground level (bgl) between high tide and low tide conditions.

In high tide conditions, the river appears to be recharging the aquifer over the entire Investigation area, with a general groundwater flow directed toward the site. In low tide conditions, as expected, the groundwater flow is generally directed toward the river.

Based on the groundwater level data, an average hydraulic gradient of about 13 % was calculated in low tide conditions, with discharge towards the river, while an inversed groundwater gradient of 3 % was measured in high tide conditions, with the aquifer generally recharging the aquifer. The gradient averaged over the 24 h shows a predominant direction towards the river, with an average gradient of 6 % in proximity of the river banks.

The interpretation of the slug tests performed showed hydraulic conductivity values ranging between 2.52×10^{-7} m/s and 4.45×10^{-6} m/s. The measured hydraulic conductivities of the Quaternary alluvium in the Investigation area have a geometric mean of $1.15E^{-06}$ m/s.

In proximity of the river, assuming a horizontal hydraulic gradient I = 0.06 (as a mean of the values reported above), an effective porosity ne = 0.015 for silt loam (Custodio and Llamas, 1996), and a horizontal hydraulic conductivity of $1.15E^{-06}$ m/s, the corresponding average horizontal groundwater darcyan velocity is equal to about 0.46 m/d or 169 m/y.

The velocities reported above shall be however carefully considered as representative only of the tidal conditions encountered during the investigations performed. In the period of observation, tidal fluctuations were of 4.25 m. These tidal fluctuations observed are to be considered within the high range. With respect of the average water level of the river, the period of observation was carried out in the low water season, which corresponds to a river flowrate in the river which can be as low as 25 % of the high water season flowrate. It can therefore be expected that the groundwater gradients measured may be considered as in the high range of the conditions that may exist with a higher river water level or with lower tides.

5.3 LNAPL distribution in soils and as separated phase

5.3.1 LNAPL Type

Separated LNAPL samples were retrieved from groundwater monitoring wells during baildown testing, and sent for identification and analysis of parameters such as viscosity, density, interfacial tension and TPH. The composition of the LNAPL samples is about 60 % aliphatic C21-C35, 20 % aromatics C21-C35 and 20 % aliphatic C16-C21. All LNAPL samples were characterized as lubricant oil, with an average density of 0.9 g/cm^3, an average kinematic viscosity at 10 °C of 138 cSt and an oil/water interfacial tension of 29 mN/m.

5.3.2 Residual saturation reference values

As a reference value, the retention factor R, expressing the residual saturation, for the vadose zone for fuel oils in fine to medium sands is indicated by Mercer and Cohen (1990) as 50 L/m^3 and for silt to fine sands as 80 L/m^3, corresponding respectively to concentrations of about 26,000 and 42,000 mg/kg (Mercer and Cohen, 1990), for a density of 0.9 g/cm^3. Mercer and Cohen (1990) also report residual LNAPL saturation values ranging from 0.15 to 0.50 for the saturated zone, and 0.10 to 0.20 for the vadose zone. These values are much larger than the maximum LNAPL saturation values measured at industrial facilities with appreciable LNAPL contamination issues (API, 2007). The initial (maximum) LNAPL saturation in a soil is a function of the LNAPL pressure history and the resulting residual LNAPL saturation has been shown to be a function of the initial LNAPL saturation (Adamski et al., 2003). The same authors recommend estimating residual LNAPL saturation as some subset of the maximum observed field LNAPL saturation, which would correspond to the maximum values of concentrations in the soils observed without presence of LNAPL. There are several potential methods of approximating field residual saturation values. One is to review soil sampling data from the LNAPL impacted zone at several locations in and near the known occurrence of free phase product. The greatest concentrations not associated with the occurrence of free product in a nearby well would be an indicator of the field residual saturation (API, 2002).

5.3.3 Field data observations

In general the highest concentrations are observed in shallow soils. TPH concentrations exceeding literature values for residual saturation in vadose soils are located mainly in the shallow vadose zone or in proximity or adjacent to the capillary fringe, with a tendency to decrease with the increase of the depth.

The lowest soil concentration in proximity of the water table, associated with presence of LNAPL shows a TPH concentration of 28,200 mg/kg and a LNAPL thickness of 0.003 m. The highest TPH soil concentration in the saturated zone not associated with presence of LNAPL is of 21,200 mg/kg in a soil classified by grain-size analysis as sandy loam (or sandy silt), which is slightly more permeable than the average of the samples.

Based on the field observations and concentration results, the field residual saturation value may be roughly estimated as comprised between 21,200 mg/kg and 28,200 mg/kg, referring to saturated zone conditions. This estimate appears to be considerably lower than the Mercer and Cohen (1990) reference value provided, which was suggesting a value of 46,000 mg/kg for the vadose zone, which generally shows much lower residual saturation than the saturated zone.

6. Baildown test analysis

The baildown testing was conducted in general accordance with the recommended API approach (Huntley, 2000). LNAPL was removed from the respective wells using bailers, and air/LNAPL and LNAPL/groundwater interfaces were measured at pre-defined intervals of time, using an interface meter.

The ES&T Baildown test software was used for the interpretation of the individual baildown tests. This software uses the van Genuchten equation (van Genuchten, 1980) modified for a three-phase system to determine the LNAPL saturation profile within the LNAPL smearing zone. The software uses the Bower and Rice Solution adapted to estimate the LNAPL conductivity, modified after Lundy and Zimmerman (1966) by including the effect of filter pack resaturation, and based on the predicted saturation profile and the measured LNAPL thickness in the well.

Relevant soil parameters, such as soil capillary properties, were estimated based on typical literature values. Identification of soils has been done using both logs and particle size distribution data. Where direct analysis was not available, physical properties of the LNAPL were estimated on the basis of the average of the analyses (for example density or viscosity) or on the basis of literature values (for example air/oil interfacial tension).

In general, baildown tests aim for a recovery of 80 % of the initial measured thickness in the well. At the Site, although the period of observation of the recovery phase after baildown was of several days, in none of the wells the target recovery was achieved.

When data were deemed suitable for interpretation, the results of the interpretation of the baildown test yielded LNAPL conductivity values ranging between about 1×10^{-8} m/sec and 1×10^{-11} m/s.

7. LNAPL body mobility assessment

7.1 Approach

The LNAPL seepage velocity is estimated using Darcy's Law using the equations presented in the Interactive LNAPL Guide Model by the American Petroleum Institute (API, 2004). The van Genuchten

(1980) capillary model is used to estimate water retention properties of the soil, which are scaled for a LNAPL-water system. The estimated LNAPL seepage velocity is compared to a de-minimus threshold of 0.3 m/y proposed by ASTM (2006), which is a threshold below which the LNAPL body is considered functionally stable. If the de-minimus velocity threshold is exceeded, there is the potential for small-scale movement of LNAPL.

The Brooks and Corey (1964) capillary model can be used to estimate the LNAPL displacement head needed for LNAPL to move laterally into soil pores not containing LNAPL. If the in-well LNAPL thickness exceeds the LNAPL displacement head, then there is the potential for LNAPL spreading into pristine soil near the water table.

7.2 Key findings

The source of contamination at the Site is related to the historical disposal of oil-filtering soils in the investigation area as a backfill. The source is therefore diffuse over almost the entire investigation area, with areas with thicker backfill than other, ranging in general between 1 and 4 m thickness. Only locally the backfill appears to be in direct contact with the shallow aquifer. Perched groundwater levels are identified at several wells in an area behind the Northern beach.

The presence of a diffuse LNAPL source over a large area is not common and is not a typical LNAPL release scenario or LNAPL conceptual model. The presence of a diffuse source prevents the decrease with distance from the point source of the LNAPL head driving force, because the source is the shallow contaminated soil which is spread across the entire area.

The vertical equilibrium model is not accurate under tidal aquifer conditions. However, considering a general stability on the measured thickness detected in the monitoring wells under low and high tide, the assessment has been performed with a “black box” approach, using an average gradient, and neglecting the effects of spreading operated by the tide as well as the gradient inversion and change of saturating conditions.

The LNAPL seepage velocity analysis reported presence of velocities higher than threshold at 7 locations, including 2 located in the core of the LNAPL body, and lower at 3 locations. The results of this analysis were performed using real site data calculated from the baildown tests, but included a calculation based on an gradient averaged over a tidal period.

The displacement head model showed results in sharp opposition to those showed by the previous model. The model considers the head necessary to enter pristine soils saturated in water, and therefore requesting a higher head to displace than air. At the Site, the higher concentrations are detected in the shallow vadose soil or in general above the capillary fringe. Above the capillary fringe, the water content decreases and LNAPL is much more readily available to enter air-filled pores. The displacement head model does therefore not appear to be accurate in assessing the potential for LNAPL mobility at the Site.

There is model and measurement uncertainty associated with the LNAPL mobility assessment, especially at a location with strong tidal influence.

8. Conclusions

The tidal influence on LNAPL movement is a subject poorly studied with limited literature available.

An evaluation of Light Non-Aqueous Phase Liquid (LNAPL) mobility was conducted at a former industrial oil refinery located along a main river under strong tidal influence. Data were evaluated in a tiered approach. The results show that the Site is subject to tidal fluctuation from more than 2 m to 0.2 m. No major geological discontinuities have been identified. In general, except at one location, the industrial fill does not appear to extend below the water table. The majority of the soil grain analyses show presence of soil classifiable as silt loam (or sandy silt). The data is confirmed by the slug testing which shows an average hydraulic conductivity of $1.15E^{-06}$ m/s.

Tidal influence appears to have a limited impact on measured NAPL thickness in the wells over time. Baildown test carried out at low and high tides do not show significant difference, except very few exceptions. Tidal influence affects strongly the gradients in the river bank area, increasing the potential for mobility of the NAPL.

TPH concentrations in soil are mainly detected in shallow soils and in proximity of the top of the capillary fringe. Very often the measured concentrations exceed residual saturation reference values adopted. Only few wells show presence of TPH concentration exceeding residual saturation reference values at the water table level. Based on the above, the majority of the LNAPL mass is located in correspondence of high TPH concentration, or in the industrial fill and in the natural soils located below these and above the capillary fringe, which has acted as a first barrier to downward migration and has possibly enhanced local lateral spreading.

All LNAPL samples analyzed are classifiable as lubricant oil, with medium to high viscosity, but general homogeneous physical characteristics. The LNAPL measured in the wells has been considered as a single LNAPL body.

LNAPL baildown tests showed in general a low to very low recovery, generally not very affected by tidal fluctuation, since the recovery time is in general much longer than the tidal cycle. None of the wells showed a recovery higher than 80 % after several days of observation. LNAPL hydraulic conductivity have been estimated as ranging between 10^{-8} and 10^{-11} m/s.

LNAPL body appears to be slowly migrating towards the river. The seepage velocity de-minimus criteria of 0.3 m/y is exceeded at 7 out of 9 wells, located both in proximity of the riverbanks or in the core of the LNAPL body. The displacement head criteria in never exceeded, but this method does not appear to be correct at estimating LNAPL mobility at this Site.

As a conclusion, the LNAPL at the Site, although presenting a limited mobility affecting its recoverability, appears to be slowly migrating under the observed conditions.

References

Adamski M., Kremesec V., Charbeneau R.J., 2003, Residual Saturation: What is it? How is it measured? How should be use it?. Petroleum Hydrocarbons Conference, National Ground Water Association, Costa Mesa, CA, August 19-20, Printed in 2005 Proceedings, 243-250.

API (American Petroleum Institute), 2002, Evaluating Hydrocarbon Removal from Source Zones and its Effect on Dissolved Plume Longevity and Concentration, API Publication 4715, <www.api.org/environment-health-and-safety/clean-water/ground-water/lnapl.aspx>, Accessed 20.03.2012.

API, 2004 API Interactive LNAPL Guide Version 2.0, Subversion 2.0.4, <www.api.org/Environment-Health-and-Safety/Clean-Water/Ground-Water/LNAPL/api-interactive-lnapl-guide.aspx>, Accessed 20.03.2012.

API, 2007, LNAPL Distribution and Recovery Model (LDRM), Volume I and II, API Publication 4760, <www.api.org/environment-health-and-safety/clean-water/ground-water/lnapl.aspx>, Accessed 20.03.2012.

ASTM (American Society for Testing and Materials), 2006, E2531-06 Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface, <www.astm.org/Standards/E2531.htm>, Accessed 20.03.2012.

Brooks, R.H., Corey, A.T., 1964, Hydraulic properties of porous media: Hydrology Papers, Colorado State University, 24 p.

CLU-IN (Hazardous Waste Clean-up Information), Mercer and Cohen 1990, Mercer and Cohen, DNAPL site evaluation, <www.clu-in.org/download/contaminantfocus/dnapl/600r93022.pdf>, Accessed 20.03.2012.

Custodio E., Llamas M.R., 1996, Underground Hydrology (Hidrologia subterranea), Vol. I, Ediciones Omega, Barcelona, Spain.

Huntley, 2000, Analytic Determination of Hydrocarbon Transmissivity from Baildown Tests, Groundwater, 38 (I), 46-52.

Lundy, D. A., L. M. Zimmerman, 1996, Assessing the recoverability of LNAPL plumes for recovery system conceptual design, In: Proceedings of the 10th Annual National Outdoor Action Conference and Exposition, National Ground Water Association, Las Vegas, NV., May 13-15, 1996., 19-34.

Van Genuchten M.Th., 1980, A closed-form equation for predicting the hydraulic conductivity of unsaturated soil, Soil Sci. Soc. Am. J., 44, 892-898.