ECG Environmental Briefs

24

Light non-aqueous phase liquids: managing site complexities

Michael Rivett (GroundH2O plus Ltd, <u>rivett@groundh2oplus.co.uk</u>), and Gary Wealthall (Geosyntec, <u>gwealthall@geosyntec.com</u>)

Managing risks posed by releases to the subsurface of light non-aqueous phase liquids (LNAPLs), such as petroleum fuels and oils, is a complex proposition of global concern. Land, groundwater and adjoining surface waters may become contaminated from poor disposal practices or accidental releases during LNAPL chemical handling, storage or transfer. This brief highlights key consider complexities to the in management of LNAPL impacted sites.

A cornerstone of site management is the development of a conceptual site model (CSM) that integrates current understanding bespoke to the site circumstance thereby enabling informed site decision making (1, 2). Whilst CSMs may often be portrayed as simplified illustrations, for example **Fig. 1**, such images often belie the inherent complexities in processes and system understanding achieved through detailed site investigation, monitoring, risk assessment and modelling efforts steered by the growing body of guidance geared to the management of LNAPL-impacted sites (1-4).

LNAPL chemical complexity

Although LNAPLs may sometimes comprise a single chemical, e.g., benzene use as an intermediate, commonly releases are of fuels/oils comprising complex mixtures of hundreds of hydrocarbons and possibly other additives, such as the fuel oxygenates MTBE (methyl-tertiary-butyl ether) (5). The overall compound assemblage influences bulk properties such as LNAPL viscosity and density that influence migration of the immiscible liquid through the porous or fractured geological sequence. The low viscosity of petrol, less than water, allows its facile subsurface migration compared to viscous oils or coal tar - creosote (CTC) products that may require decades for released NAPL to attain a quasi-steady state subsurface distribution. Whilst LNAPLs are defined to be less dense than water and 'float' upon the (ground)water table, densities of CTC products approaching unity cause their

inherent chemical composition to control if they are a LNAPL or else a D(dense)NAPL able to penetrate as an immiscible phase below the water table (1, 5).



Fig. 1. LNAPL conceptual models (after CL:AIRE, 2014) (1)

Multiphase flow complexity

Migration of LNAPL released into the subsurface represents a complex 'multiphase flow' problem in which LNAPL, gas and water phases are present and each able to migrate within the porous and, or fractured (fissured) subsurface. Whilst LNAPL is expected to generally invade more permeable geological horizons and initially migrate downward towards the water table to spread laterally at that interface as a buoyant LNAPL (Fig. 1a), significant nuances control the distribution 'architecture' of the LNAPL source zone that develops. Complexities include LNAPL migration sensitivities to its density, viscosity, composition and wettability, the detailed geological permeability field and resident saturation of pore spaces by air and water phases, mode of release (e.g., drip versus catastrophic), and variations over time (e.g. of the water table) (2).

Geological complexity

The geological subsurface is complex. LNAPL migration and fate may vary significantly between the different aquifer types, such as chalk, sandstone and limestone used to supply groundwater in the UK, alluvial aquifers connecting to surface waters, and low permeability aquitard units such as clays or mudstones that may offer significant protection of underlying aquifer units that is not always guaranteed (6). Fig 1 contrasts LNAPL fate within a fractured sandstone that is porous compared to one that is cemented where the LNAPL is unable to directly enter the sandstone matrix; entry of contaminants there being restricted to diffusive transport in the aqueous phase. Example LNAPL conceptual models of the geological systems named above (and more) may be found in CL:AIRE (2014) (1).

Chemical partitioning complexity

The subsurface LNAPL source zone formed may deplete via chemical partitioning. This involves dissolution that continuously generates a migrating dissolved-phase groundwater plume; alongside, LNAPL chemical volatilisation into the soil gas, forming vapour plumes posing vapour intrusion (VI) risks. These partitioning processes may occur simultaneously and their rates may be significantly influenced by the additional complexity of continual LNAPL redistribution on a (seasonally) fluctuating water table. Individual chemical depletion rates will vary over time being controlled by both their pure-phase solubility and vapour pressure, but also changing LNAPL mole fraction (Raoult's law often being used as an approximation (5)). Although benzene, toluene, ethylbenzene, and xylenes (BTEX) and fuel oxygenates often form key risk drivers and the most soluble/volatile components preferentially lost, LNAPL mass is often so large that source depletion may still require decades, especially where mass occurs at the interface with, or has diffused into, low permeability units (e.g., clays).

Attenuation process complexity

A saving grace is that many hydrocarbons are prone to biodegradation in the subsurface which may result in the 'natural attenuation' (NA) of migrating dissolved-phase and vapour plumes. Given appropriate conditions, notably sufficient supply of electron acceptors (dissolved oxygen, nitrate, sulfate, etc.) and suitable microbial communities, then biodegradation may occur to innocuous products and plumes become limited in extent, eventually shrinking as source zone inputs decline (1-5). Whilst biodegradation has hitherto often been assumed to occur on contaminant in the aqueous phase, there is growing evidence from natural sourcezone depletion (NSZD) studies that biodegradation may occur within the LNAPL body itself. Moreover, the significance of methanogenesis, gaseous-phase mass loss, and biodegradation in the unsaturated zone mitigating contaminant breakthrough at ground surface have been significantly underappreciated hitherto (7).

Problem synthesis and management

As stated at outset, at the heart of the problem synthesis is the continued iteration of the LNAPL CSM. This is central to the management of a specific site scenario. It is obvious from the above that several lines of complexity need to be interrogated and synthesised to establish an advanced CSM and its detailed reporting. Although detail is beyond the scope of this brief, it is important to recognise the key roles of site investigation and on-going monitoring of sites in the evolution of the LNAPL CSM that should continue during the, quantitative assessments of risks, including analytical/numerical modelling efforts, and the implementation, as required, of site remedies to lower risks to acceptable levels and successfully manage and secure progression to site closure. Regarding these aspects, the reader is referred to the citations made (1-7) and many references therein. Finally, it is recognised in closing that a wealth of almost 50 years' experience and research dating from the 1970s is now available to draw upon in our management of LNAPL-contaminated sites.

References

- 1. CL:AIRE, 2014. An illustrated handbook of LNAPL transport and fate in the subsurface. CL:AIRE, London. ISBN 978-1-905046-24-9. www.claire.co.uk/LNAPL
- Tomlinson D, Rivett MO, Wealthall GP, Sweeney R (2017). Understanding complex LNAPL sites: Illustrated handbook of LNAPL transport and fate in the subsurface. J. Environ. Manage., 204, 748-756. https://doi.org/10.1016/i.jenyman.2017.08.015
- ITRC (2018). LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies. LNAPL-3. Washington, D.C.: Interstate Technology & Regulatory Council. LNAPL Update Team. <u>https://lnapl-3.itrcweb.org</u>
- CL:AIRE (2017). Petroleum Hydrocarbons in Groundwater: Guidance on assessing petroleum hydrocarbons using existing hydrogeological risk assessment methodologies. CL:AIRE, London. ISBN 978-1-905046-31-7. www.claire.co.uk/phg
- 5. Leharne S (2017). Non-aqueous phase liquids: properties, risk reduction and remediation. ECG Environmental Brief No. 15. https://www.envchemgroup.com/eb15-non-aqueousphase-liquids.html
- White RA, Rivett MO, Tellam JH (2008). Paleo-roothole facilitated transport of aromatic hydrocarbons through a Holocene clay bed. Environ. Sci. Technol., 42(19): 7118-7124. http://dx.doi.org/10.1021/es800797u
- Garg S, Newell CJ, Kulkarni PR, King DC, Adamson DT, Renno MI, Sale T (2017). Overview of natural source zone depletion: Processes, controlling factors, and composition change. Groundwater Monit. R., 37: 62–81. http://dx.doi.org/10.1111/gwmr.12219