LNAPL Transport and Fate in the Subsurface

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Acronyms

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BTEX	Benzene, toluene, ethylbenzene and xylenes
CL:AIRE	Contaminated Land: Applications in Real Environments
COPC	Contaminants of potential concern
CPT	Cone penetrometer testing
CSM	Conceptual site model
Defra	Department for Environment, Food and Rural Affairs
DNAPL	Dense non-aqueous phase liquid
EA	Environment Agency
ETBE	Ethyl tertiary-butyl ether
FID	Flame ionisation detection/detector
GC	Gas chromatograph/chromatography
GTL	Gas-to-liquid
ISCO	*In situ* chemical oxidation
ITRC	Interstate Technology and Regulatory Council
LIF	Laser-induced fluorescence
LNAPL	Light non-aqueous phase liquid
MIP	Membrane interface probe
MNA	Monitored natural attenuation
MTBE	Methyl tertiary-butyl ether
NAPL	Non-aqueous phase liquid
NFEC	Naval Facilities Engineering Command
NSZD	Natural source zone depletion
PAH	Polycyclic aromatic hydrocarbons
PID	Photoionisation detection/detector
PITT	Partitioning interwell tracer testing
PRB	Permeable reactive barrier
SPE	Solid phase extraction
SVE	Soil vapour extraction
TAME	Tertiary-amyl methyl ether
TBA	Tert-butyl alcohol
TCEQ	Texas Commission on Environmental Quality
TEX	Toluene, ethylbenzene and xylenes
TPH	Total petroleum hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
TPH-D	Diesel range total petroleum hydrocarbons
TPH-G	Gasoline range total petroleum hydrocarbons
USEPA	United States Environmental Protection Agency
UST	Underground storage tank
VER	Vacuum enhanced recovery
VI	Vapour intrusion
VOC	Volatile organic compound

1. Introduction

This course presents best-practice guidance for the assessment and remediation of light non-aqueous phase liquids (LNAPLs) in the subsurface. It is anticipated to be of benefit to not only practitioner and supporting research communities, but also serve as an educational resource to those having a more peripheral interest (noting a glossary of key technical terms is provided). It aims to provide a mix of technical detail and practical conceptualisation of the problem that is relevant to real world scenarios. It also serves to provide a convenient interface to a wealth of modern and established research, guidance and case study literature.

LNAPLs are hydrophobic liquid organic chemicals that are immiscible with water and are less dense than water. A LNAPL hence exists as a separate organic liquid phase when in contact with water and is able to ‘float’ upon that aqueous-phase liquid. They are amongst the most frequently encountered organic contaminants in the subsurface environment. They include a wide range of substances, but the most common types are fuels and oils, such as petrol (gasoline), diesel, heating oils and jet fuel (kerosene). LNAPL releases to ground can result from a range of release mechanisms. As illustrated in Fig. 1.1, these include accidental leakage from above ground and underground storage tanks (USTs) and associated pipelines as well as accidental release during handling, storage or transfer at fuel manufacturing facilities, refineries, bulk-product terminals, petrol filling stations, airports, military bases, and from smaller scale storage at domestic properties, industrial facilities and farms (CL:AIRE, 2002; Molins *et al*., 2010; USEPA, 2009; USGS, 1998). Whilst the vast majority of LNAPL releases originate from (near) ground surface, occasionally LNAPL sources may occur at depth below the water table and pose risks of buoyant LNAPL rise into an overlying groundwater resource. This may include natural LNAPL seeps from deep strata, but also risks of anthropogenic origin. For example, risks posed by potential release of LNAPL from degraded Intermediate Level (nuclear) Waste stored in an engineered geological disposal facility at depth where LNAPL fate in the near-field hydrogeological environment requires consideration (Benbow *et al*., 2014; Wealthall, 2002).

Figure 1.1. Example of LNAPL releases showing a leaky underground storage tank (left) and LNAPL impact to a surface-water receptor (right) (Courtesy of N. Clarke and M.O. Rivett respectively).

Unlike dense non-aqueous phase liquids (DNAPLs) that sink in water, LNAPLs are less dense than water and when released to the subsurface they migrate through partially (water) saturated strata until they reach the water table, which impedes (but not completely prevents) their migration deeper due to both increasing water content and associated buoyancy forces arising from the LNAPL-water fluid density contrast. Lateral spread of LNAPL near the water table is determined principally by the subsurface geology, size of the LNAPL release, as well as physical-chemical properties of the LNAPL.

Mobility of the LNAPL is influenced by the size of the release and the fluid's viscosity. Low viscosity LNAPL releases (such as petrol) may stabilise within weeks to months, whereas high viscosity LNAPLs (such as heating oil or crude oil) flow more slowly for longer periods and may require months to years for the LNAPL to gradually stabilise. The LNAPL distribution that accumulates in the subsurface is typically termed the 'source zone' of contamination. It comprises both immobile residual LNAPL, which is trapped in pore space by capillary forces, and potentially mobile LNAPL which exists as a continuous liquid across interconnected pores and is able to migrate when subjected to a sufficient driving head. The latter often manifests as a layer of LNAPL (e.g., oil or fuel) distributed across the water table-capillary fringe interface due to the LNAPL buoyant nature. Some penetration of LNAPL below that interface is, however, possible (Fig. 1.2).

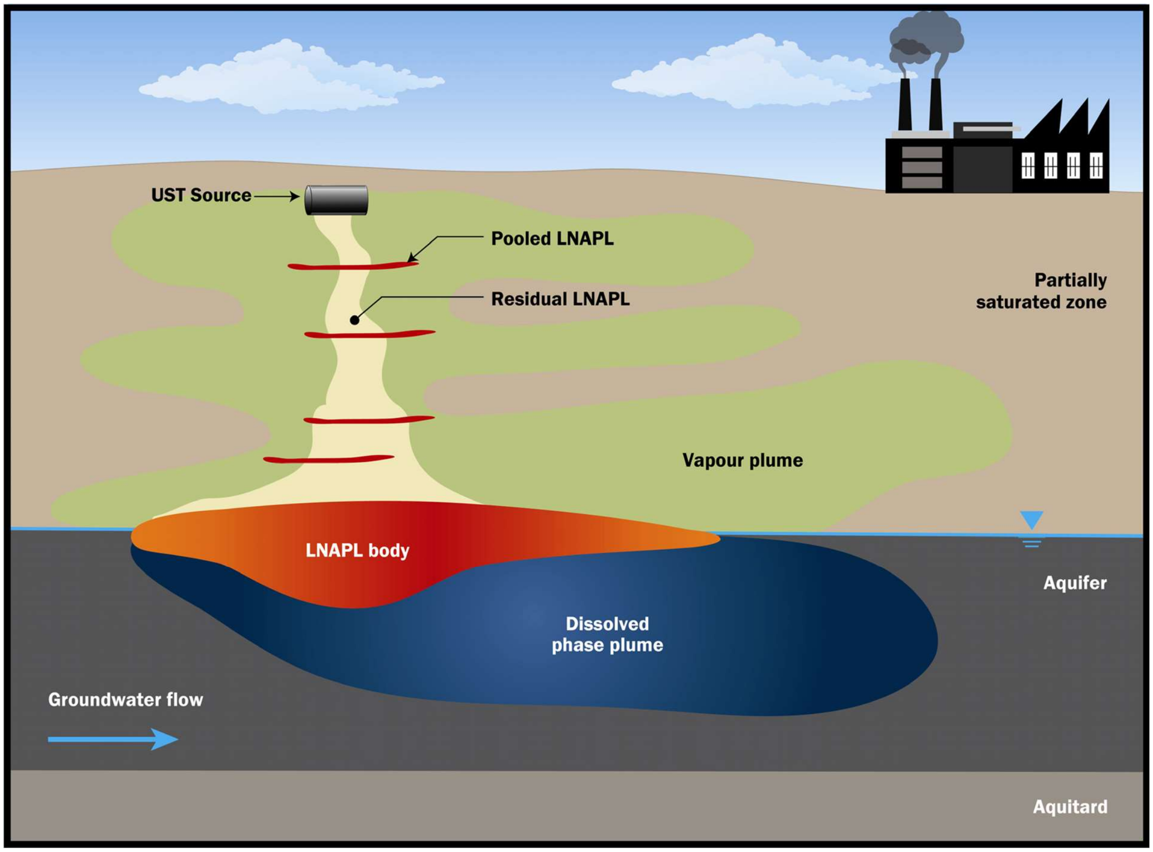

Figure 1.2. Illustrative conceptual model of a LNAPL release to the subsurface.

The physical-chemical properties of individual compounds within the contaminant mixture control rates of partitioning (mass transfer) from the LNAPL to the gas and aqueous phases. This transfer leads to the development of vapour-phase plumes in the unsaturated (vadose, or more accurately partially saturated) zone above the water table and shallow dissolved-phase plumes in groundwater laterally flowing beneath the water table. These processes are conceptualised in Fig. 1.2.

This document aims to provide an accessible overview of LNAPL behaviour in soil and groundwater, including a series of illustrative conceptual models of LNAPL in different hydrogeological environments, to establish:

- better conceptual understanding of LNAPL transport and fate in the subsurface, on which risk-management strategies can be developed;
- more effective site characterisation and robust risk prediction;
- risk-based management of LNAPL releases that is more sustainable; and
- improved understanding of where and/or when specific LNAPL remedial techniques are likely to be effective in performance and cost.

2. Types of LNAPL and their properties

2.1. Introduction

The term LNAPL describes a class of liquid organic chemicals that are characterised by:

- immiscibility with water (hydrophobicity);
- densities which are less than that of water; and
- complex chemical compositions in most cases.

These defining characteristics have a direct impact upon their behaviour in the geological subsurface when released at sites. The most frequently encountered LNAPLs are complex mixtures of organic compounds, such as fuels and oils. Such LNAPLs are compositionally complex containing aliphatic and aromatic hydrocarbons in varying ratios. They may be further formulated with a range of additives that enhance and extend their performance as fuels or lubricants. This section provides details of the types and uses of commonly encountered LNAPLs, elaborating on the key physical-chemical properties - such as density, viscosity, interfacial tension (against water), composition, aqueous solubility, vapour pressure and wetting behaviour - that influence their environmental fate. The variability in properties of some typical LNAPLs is illustrated in Table 2.1. The diversity in LNAPL properties occurring across the wide range of fuels and oils leads to contrasting fate and transport in the subsurface. It is hence important to obtain available literature property data in making an assessment; such data may be found, for example, in Mercer and Cohen (1990), the API Interactive LNAPL Guide (API, 2006a), and the API Parameters Database (API, 2006b).

Table 2.1. Typical fuel LNAPLs: uses and physical properties (at 15°C) (NFEC, 2010).

Fuel type	Fuel use	Density (g/cm^3)	Viscosity (cP)	Boiling point range (°C)	Interfacial tension (mN/m)
Petrol	Road vehicle fuel	0.67-0.8	0.62	38-204	52
AVGAS	Aviation spirit for piston engines	0.71	2.3	33-170	37
Jet A-1	Civil aviation jet fuel	0.804	2-3	145-300	-
JP-4	Military jet fuel	0.75	1.0	60-270	50
JP-5	Military jet fuel	0.82	2.0	176	-
JP-8	Military jet fuel	0.78-0.84	2.0	205-300	-
Kerosene	Paraffin - used for heating and lighting	0.81	2.3	151-301	47-49
Diesel	Transport fuel	0.87	2.7	150-370	50
Bunker C	Fuel oil used for ship propulsion	0.9-1.1	45,030	>177	40
Tar / bitumen	Tarmac, road surfacing	1.15	-	-	-