LNAPL Transport and Fate in the Subsurface

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Module 1: Introduction

Learning Objectives

By the end of this section, you will be able to:

- **Identify** the physical-chemical properties that distinguish LNAPLs from DNAPLs.
- **Evaluate** the factors influencing the lateral spread and stabilization timeframes of subsurface LNAPL releases.
- **Select** appropriate conceptual models to describe the formation of dissolved-phase and vapour-phase plumes.

Executive Summary: LNAPLs are hydrophobic, low-density organic contaminants—primarily fuels and oils—that present complex subsurface transport challenges. Because they float on the water table, their migration is governed by buoyancy and viscosity, eventually forming "source zones" of both mobile and immobile residual liquids that generate secondary vapour and dissolved-phase plumes.

LNAPL Fundamentals

Light non-aqueous phase liquids (LNAPLs) are liquid organic chemicals characterized by two defining physical traits: they are **hydrophobic** (immiscible with water) and **less dense** than water. Consequently, LNAPL exists as a distinct organic phase that "floats" upon aqueous liquids. Commonly encountered LNAPLs include:

- **Petrol (Gasoline)**
- **Diesel and Heating Oils**
- **Jet Fuel (Kerosene)**

Release Mechanisms and Risks

Subsurface releases typically occur near the ground surface through several mechanisms:

- **Infrastructure Failure**: Accidental leakage from above-ground or **underground storage tanks (USTs)** and associated pipelines.
- **Operational Handling**: Spills during transfer or storage at refineries, bulk terminals, airports, and military bases.
- **Deep-Strata Risks**: Occasionally, LNAPL sources occur at depth below the water table, such as natural seeps or releases from degraded nuclear waste in geological disposal facilities, requiring consideration of buoyant rise into groundwater resources.

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).

Subsurface Transport and Distribution

Unlike **DNAPLs**, which sink, LNAPLs migrate downward through partially saturated strata until they reach the **water table**. The water table acts as a barrier, impeding deeper migration due to increased water content and **buoyancy forces**.

Key Drivers of Distribution

- **Lateral Spread**: Determined by subsurface geology, release volume, and the physical-chemical properties of the fluid.
- **Stabilization Timeframes**: Heavily dependent on **viscosity**.
    - **Low Viscosity (e.g., Petrol)**: May stabilize within weeks to months.
    - **High Viscosity (e.g., Crude Oil)**: Flows slower and may require months to years to reach a stable state.

The Contamination "Source Zone"

The accumulated LNAPL in the subsurface is known as the **source zone**. It is categorized into two physical states:

1. **Immobile Residual LNAPL**: Trapped in pore spaces by **capillary forces**.
2. **Potentially Mobile LNAPL**: Exists as a continuous liquid across interconnected pores, capable of migrating under a sufficient **driving head**.

This mobile phase typically forms a layer across the water table-capillary fringe interface, though some penetration below the interface is possible.

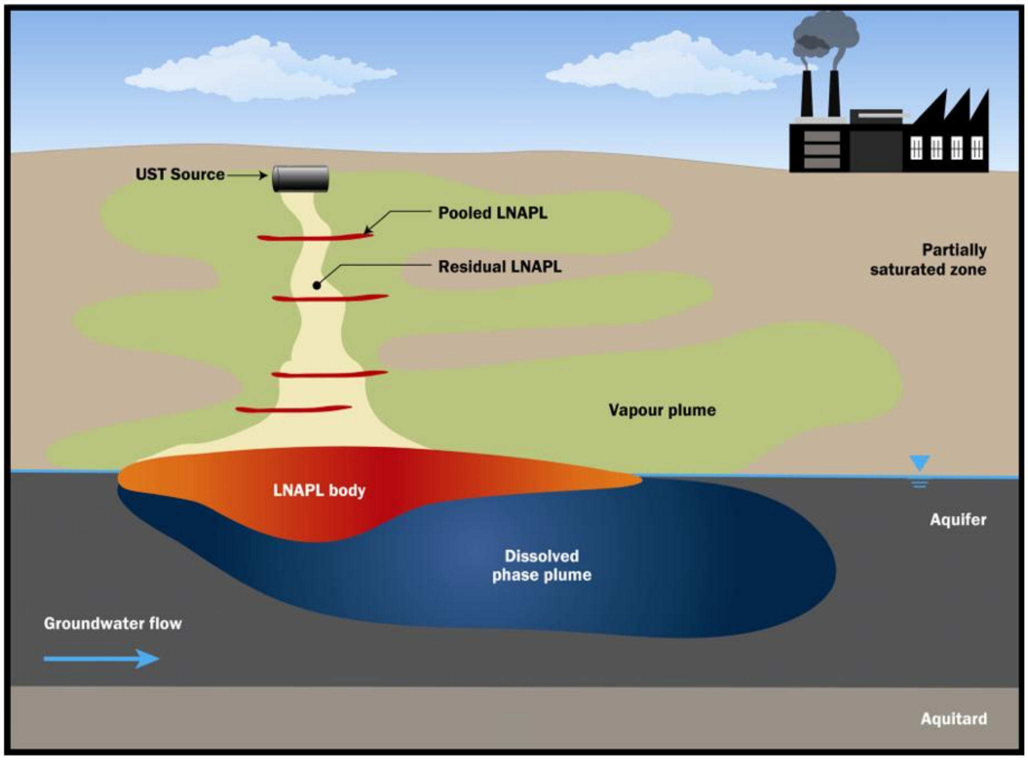


Figure 1.2. Illustrative conceptual model of a LNAPL release to the subsurface.

Mass Transfer and Plume Development

The partitioning of individual compounds from the LNAPL mixture creates secondary contamination plumes:

- **Vapour-phase Plumes**: Develop in the unsaturated (vadose) zone above the water table.
- **Dissolved-phase Plumes**: Form in groundwater flowing laterally beneath the water table.

💡 **Design Tip**: Effective risk-management strategies must be built upon a robust conceptual understanding of how LNAPL transport and fate vary across different hydrogeological environments.

Checkpoint Quiz

1. **Which factor is the primary reason LNAPLs accumulate near the water table rather than sinking to the bottom of an aquifer?**
    a) High chemical solubility
    b) Fluid density contrast and buoyancy forces
    c) Rapid biodegradation
    d) Low molecular weight

Answer: (b). LNAPLs are less dense than water, causing buoyancy forces to impede their downward migration once they reach the saturated zone.

2. **How does viscosity affect the stabilization of a LNAPL source zone?**
    a) Higher viscosity leads to faster stabilization within days.
    b) Viscosity has no effect on stabilization timeframes.
    c) High viscosity fluids flow more slowly and can take years to stabilize.
    d) Low viscosity fluids remain mobile indefinitely.

Answer: (c). High viscosity LNAPLs, such as heating or crude oils, flow more slowly and require significantly longer periods—months to years—to stabilize compared to low-viscosity fluids like petrol.

3. **A "Source Zone" is defined as containing which of the following?**
    a) Only dissolved-phase contaminants in groundwater
    b) Only gas-phase contaminants in the vadose zone
    c) Both immobile residual LNAPL and potentially mobile continuous liquid
    d) Only petrol and diesel fuels

Answer: (c). The source zone comprises both residual LNAPL trapped by capillary forces and mobile LNAPL that can migrate through interconnected pores

Module 2: Types of LNAPL and Their Properties

Learning Objectives

By the end of this section, you will be able to:

- **Identify** the physical-chemical properties that govern LNAPL behavior in the subsurface.
- **Calculate** the threshold capillary (entry) pressure for LNAPLs using interfacial tension, contact angle, and pore radius.
- **Evaluate** how multi-component mixtures and fuel additives (like ethanol and surfactants) alter LNAPL mobility and solubility.

Executive Summary: LNAPL behavior is driven by the interplay of density, viscosity, and interfacial tension. While most LNAPLs are complex mixtures derived from crude oil, their environmental fate is significantly altered by "effective solubility" in water and the presence of additives that can reduce capillary entry pressures, potentially facilitating more rapid or extensive migration than pure hydrocarbons.

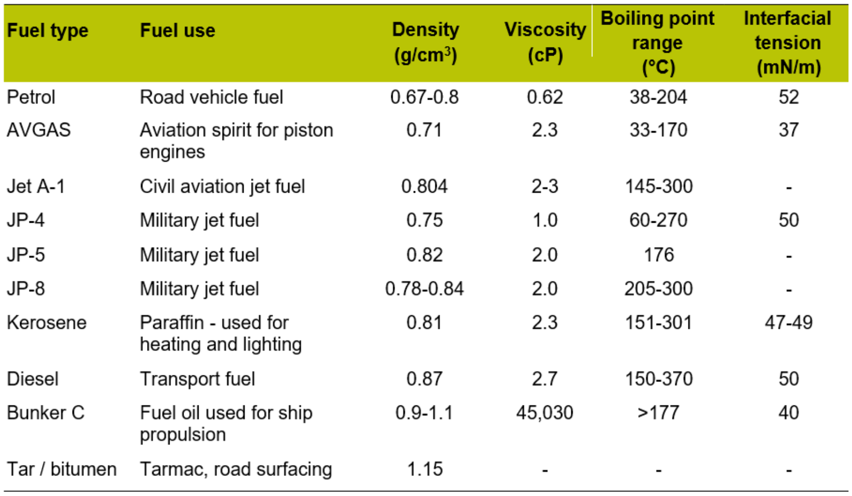
Introduction

The term **LNAPL** describes a class of liquid organic chemicals characterized by:

- **Immiscibility** with water (hydrophobicity).
- **Densities** less than that of water.
- **Complex chemical compositions** in most cases.

These traits directly impact subsurface behavior. Most frequently encountered LNAPLs are complex mixtures of aliphatic and aromatic hydrocarbons, often formulated with additives to enhance performance. Variability in these properties (Table 2.1) leads to contrasting fate and transport.

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	-	-	-