# DNAPL 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 properties and common chemical classes of Dense Non-Aqueous Phase Liquids (DNAPLs).
- **Evaluate** the historical and technical factors that contributed to the delayed recognition of DNAPL contamination.
- **Assess** the long-term environmental risks and remediation challenges associated with DNAPL presence in various hydrogeological environments.

*Executive Summary:* DNAPLs are industrial organic liquids denser than water that pose significant long-term contamination risks due to their ability to migrate deep below the water table. Historically misunderstood and difficult to remediate, these substances require specialized site investigation and risk assessment approaches to manage their toxicity and persistence in soil and groundwater.

## Understanding DNAPL Fundamentals

**Dense non-aqueous phase liquids (DNAPLs)** represent a category of organic liquids characterized by a density greater than water and limited solubility. Because they are immiscible, they exist in the subsurface as a distinct fluid phase separate from both water and air.

## Key Characteristics and Behavior

- **Subsurface Persistence:** DNAPLs exist as a separate phase and only slowly dissolve into flowing groundwater.
- **Deep Migration:** Unlike **light non-aqueous phase liquids (LNAPLs)** like petrol, which float, DNAPLs migrate to significant depths below the water table.
- **Contamination Zones:** A surface release can lead to the long-term contamination of both **unsaturated** and **saturated** zones.
- **Plume Generation:** As they dissolve, they give rise to aqueous phase plumes that spread through the aquifer.

## Common Industrial DNAPLs

- **Timber Treating Oils:** Such as creosote.
- **Electrical/Insulating Oils:** Containing polychlorinated biphenyls (PCBs).
- **Coal Tar:** Derived from industrial gas processes.
- **Chlorinated Solvents:** Including trichloroethene (TCE) and tetrachloroethene (PCE).

## Historical Context and Awareness

While DNAPLs have seen widespread industrial use since the start of the 20th century, their environmental significance was not fully recognized until the **1980s**. This delay in awareness stemmed from several critical factors:

## Technical and Regulatory Barriers

- **Analytical Limitations:** Equipment required to detect low concentrations of organic compounds in groundwater was not widely available until recently.
- **Misleading Guidance:** Material safety data sheets (MSDS) from the 1940s to the 1970s often suggested spreading waste solvents on dry ground for evaporation as an "acceptable practice".
- **Incomplete Vapor Knowledge:** Early guidance recognized chemical volatility but failed to account for rapid infiltration into the subsurface.
- **Societal Factors:** A general lack of understanding regarding groundwater's importance as a potable supply led to the widespread use of shallow soil systems for waste disposal.

## Global and UK Environmental Impact

There are potentially thousands of DNAPL-impacted sites in the UK, North America, and continental Europe. Many UK sites involve legacy contamination from the mid-20th century, following the post-World War II industrial expansion.

## Remediation and Risk Challenges

- **Technical Difficulty:** Experience from the last 20 years shows that these sites are exceptionally difficult to investigate and challenging to remediate.
- **Geological Penetration:** DNAPLs can penetrate fractured rock and clay.
- **Longevity:** In most environments, it takes many decades for natural dissolution to dissipate DNAPL sources.
- **Toxicity:** Most DNAPL compounds are toxic to mammals and other fauna, making them a major environmental concern.

⚠️ **Safety Constraint:** PEs must recognize that the discipline of groundwater and soil contamination by hazardous organic liquids is evolving continuously. Always consult the most recent advances in understanding and approaches when conducting risk assessments.

💡 **Design Tip:** Site investigators should account for the "young" nature of this scientific field compared to other engineering disciplines. Historical data from before the 1980s likely underestimates DNAPL presence due to the lack of adequate detection technology at that time.

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*Checkpoint Quiz*

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1. **Which property primarily distinguishes the subsurface migration of DNAPLs from LNAPLs?**
    a) Total solubility in groundwater
    b) Density relative to water
    c) Volatility in the unsaturated zone
    d) Toxicity to mammals

**Answer:** (b). DNAPLs are denser than water, allowing them to migrate below the water table, whereas LNAPLs are less dense and float.

2. **Why was DNAPL contamination largely unrecognized by the regulatory community prior to the 1980s?**
    a) DNAPLs were not used in industry until the late 20th century.
    b) DNAPLs were believed to be fully miscible with water.
    c) Analytical equipment for detecting low organic concentrations was not widely available.
    d) Most DNAPLs were considered non-toxic before 1970.

**Answer:** (c). A lack of recognition was partly due to the recent development and availability of sensitive analytical methods

3. **What is a primary challenge in the natural dissipation of DNAPL sources in the subsurface?**
    a) They evaporate too quickly to be measured.
    b) They only contaminate the unsaturated zone.
    c) Natural groundwater dissolution can take many decades to dissipate the source.
    d) They are unable to penetrate clay or fractured rock.

**Answer:** (c). Due to low solubility and deep penetration, DNAPL sources persist for decades.

# Module 2: Types of DNAPLs

## Learning Objectives

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

- **Select** appropriate diagnostic parameters (density, viscosity, solubility) to characterize different classes of DNAPLs found at industrial sites.
- **Identify** the industrial processes and historical applications associated with creosote, coal tar, PCBs, and chlorinated solvents.
- **Evaluate** the subsurface migration potential and attenuation characteristics of single versus multi-component DNAPLs.

*Executive Summary:* DNAPLs are primarily categorized into four classes: creosote, coal tar, PCBs, and chlorinated solvents, each possessing distinct physical behaviors in the subsurface. Their migration timescales range from rapid (chlorinated solvents) to extremely persistent (coal tar and creosote), driven largely by density and viscosity.

## Design Fundamentals: Creosote

**Creosote** is a complex mixture of coal tar distillates and was historically ubiquitous in treating wood products like railway sleepers and telegraph poles. It remains in use for specialized timber operations and roofing/road tars.

## Physical Characteristics and Migration Behavior

- **Composition:** Primarily polycyclic aromatic hydrocarbons (PAHs) and phenolic compounds. It is often blended with up to 50% carrier fluid, such as diesel, which impacts its final density.
- **Density:** Typically ranges between **1,010 and 1,130 kg/m³**. As one of the least dense DNAPLs, its downward gravity-driven migration is relatively slow.
- **Viscosity:** Ranges between **20 and 50 cP**. This high viscosity facilitates long migration timescales; creosote can remain mobile for **50 to 60 years** post-release.

**Groundwater Impact:** Investigators typically use a subset of compounds—naphthalene, benzo[a]pyrene, and phenanthrene—to characterize water quality. Because these compounds are highly hydrophobic, they sorb strongly to soil and rock, often resulting in aqueous plumes that do not migrate far beyond the DNAPL source.

**Table 1: Possible components of creosote (adapted from Cohen and Mercer, 1993)**

| Acid extractable | Base/neutral | Heterocyclic |
|---|---|---|
| **phenol** | naphthalene | quinoline |
| **cresols** | methylnaphthalenes | isoquinoline |
| **pentachlorophenol** | dimethylnaphthalenes | carbazole |
| **xylenols** | biphenyl | 2,4-dimethylpyridine |
| **2,3,5-trimethylphenol** | acenaphthene | benzo[b]thiophene |
| | fluorene | dibenzothiophene |
| | phenanthrene | dibenzofuran |
| | anthracene | |
| | fluoranthene | |
| | pyrene | |
| | chrysene | |
| | anthraquinone | |
| | 2,3-benzo[b]pyrene | |
| | methylanthracene | |
| | benzo[a]pyrene | |
| | diphenyldimethylnaphthylene | |
| | diphenyloxide | |

## Design Fundamentals: Coal Tar

**Coal tar** is a byproduct of coal gasification (manufactured gas operations) and blast furnace coke production. It is a complex mixture containing light to heavy oil fractions, anthracene oil, and pitch.

**Technical Constraints:**

- **Density: 1,010 to 1,100 kg/m$^3$**.
- **Viscosity: 20 to 100 cP**.
- **Persistence:** Similar to creosote, its low density and high viscosity mean it may still be migrating as a DNAPL decades or even a century after initial release.

**Groundwater Characterization:** Key indicators include **BTEX compounds** (benzene, toluene, ethylbenzene, xylenes) and PAHs (benzo[a]pyrene, naphthalene, phenanthrene).

## Design Fundamentals: Polychlorinated Biphenyls (PCBs)

**PCBs** consist of 209 congeners manufactured mainly by Monsanto (under the trade name **Aroclor**) between 1930 and 1977. They were primarily used in capacitors, transformers, and heavy industrial applications due to their chemical stability.