# DNAPL Transport and Fate in the Subsurface

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# Introduction

Dense non-aqueous phase liquids (DNAPLs) that have been widely used in industry since the beginning of the 20th century. DNAPLs are only slightly soluble in water and therefore exist in the subsurface as a separate fluid phase immiscible with both water and air. Common types of DNAPLs include timber treating oils such as creosote, transformer and insulating oils containing polychlorinated biphenyls (PCBs), coal tar, and a variety of chlorinated solvents such as trichloroethene (TCE) and tetrachloroethene (PCE). Unlike light non-aqueous phase liquids (LNAPLs) such as petrol and heating oil (which are less dense than water), DNAPLs (which are denser than water) have the ability to migrate to significant depths below the water table where they slowly dissolve into flowing groundwater, giving rise to aqueous phase plumes.
A release of DNAPL at the ground surface can therefore lead to long-term contamination of both the unsaturated and saturated zones at a site.

Although DNAPLs have been produced and utilised widely since the beginning of the 20th century, their importance as soil and groundwater contaminants was not recognised until the 1980s. This lack of recognition by the industrial, regulatory and research communities was partly due to the fact that the analytical methods and equipment required to detect low concentrations of organic compounds in groundwater were not widely available or used until relatively recently. In addition, some chemical manufacturer material safety data sheets distributed from the 1940s until the early 1970s suggested that ‘acceptable practice’ for the disposal of waste chlorinated solvents and the residues of distillation was to spread them onto dry ground to allow them to evaporate. These early material safety data sheets recognised the volatile nature of many DNAPL chemicals, but they did not recognise the ability of DNAPLs to infiltrate rapidly into the subsurface, causing soil and groundwater pollution. Additional factors contributing to the relatively late awareness of the impact of DNAPLs on soil and groundwater quality include society’s general lack of understanding of the importance of groundwater as a supply of potable water, and the widespread use of shallow soil systems as a location to dispose of unwanted materials.

There are potentially several thousand DNAPL-impacted sites throughout the UK. Many of these sites are affected by releases of DNAPL that took place in the middle of the 20th century (coincident with the rise in industrial activity post World War II), as well as by more recent discharges. In addition, there are thousands of DNAPL-impacted sites in North America, continental Europe and other industrialised areas of the world. Experience from the past 20 years has demonstrated that DNAPL sites are difficult to investigate and challenging to remediate. DNAPL can penetrate fractured rock and clay and, in most hydrogeological environments, many decades are required for natural groundwater dissolution to dissipate DNAPL sources. DNAPL impacted soil and groundwater are of major concern in the UK; most DNAPL compounds have been found to be toxic to mammals and other fauna. Certain DNAPL compounds are highly mobile in the subsurface and groundwater forms an integral part of the hydrologic cycle as well as an important resource in its own right.

The purpose of this course is to provide a user-friendly overview of the nature of DNAPL contamination in a UK context. It is intended to assist site investigators, site owners and regulators in conducting site investigations and risk assessments, and in selecting remediation approaches. While this course reflects the state-of-the-art at the time of publication, it should be noted that the discipline of groundwater and soil contamination by hazardous organic liquids is evolving continuously and is relatively ‘young’ in comparison with many other areas of science and engineering.

# Types of DNAPLS

In general, a DNAPL is defined as a heavier-than-water organic liquid that is only slightly soluble in water. The acronym was first introduced in the USA during litigation proceedings in New York State in the late 1970s. The primary classes of DNAPLs include creosote, coal tar, PCB oils and chlorinated solvents. Other, less frequently encountered DNAPLs include mercury and certain crude oils. All DNAPLs can be characterised by their density, viscosity, interfacial tension with water, component composition, solubility in water, vapour pressure and wettability. These terms are used throughout this course; a short description of each is given in the glossary in Section 11.

## 2.1 Creosote

Creosote is composed of various coal tar distillates and was commonly used to treat wood products such as railway sleepers and telegraph poles. It is still used today in certain timber-treating operations and as a component of roofing and road tars. Creosote contains many hydrocarbons, primarily polycyclic aromatic hydrocarbons (PAHs) and phenolic compounds. **Table 1** lists a number of possible components of creosote. Creosote may be blended, however, with up to 50% of a carrier fluid such as diesel fuel prior to use. The density of creosote typically ranges between 1,010 and 1,130 kg/ m$^3$, depending on the amount and type of any carrier fluid. Creosote is therefore one of the least dense DNAPLs of environmental interest. It often takes a long time for movement to cease following initial release into the subsurface because creosote is only slightly denser

**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 |  |

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than water and has a relatively slow downward (gravity-driven) migration.

The relatively high viscosity of creosote, which typically ranges between 20 and 50 cP, also facilitates the long migration timescale. It is not uncommon to encounter sites where creosote DNAPL is still moving following its introduction to the subsurface as much as 50 or 60 years earlier.

In assessing the impact to groundwater, most investigators select a subset of creosote compounds to characterise water quality. These may include naphthalene, benzo[a]pyrene and phenanthrene. Because some of these compounds are typically very hydrophobic, they tend to sorb strongly to soils and rock. This means that aqueous plumes of certain contaminants associated with creosote sources will be heavily attenuated relative to the rate of groundwater flow, and therefore may not have migrated far beyond the spatial extent of the DNAPL creosote.

## 2.2 Coal tar

Like creosote, coal tar is a complex mixture of hydrocarbons produced through the gasification of coal. Coal tar was historically produced as a by-product of manufactured gas operations up until approximately 1950, and is currently still produced as a by-product of blast furnace coke production. Coal tar contains hundreds of hydrocarbons, including light oil fractions, middle oil fractions, heavy oil fractions, anthracene oil and pitch. The density of coal tar typically ranges from 1,010 to 1,100 $kg/m^3$ and the viscosity from 20 to 100 cP. The relatively low density and high viscosity of coal tar implies that it may still be migrating as a DNAPL at sites where it was introduced to the subsurface many decades (or even a century) earlier. With respect to the impact on groundwater, most investigators typically select a subset of compounds to assess the impact on water quality. These may include the suite of BTEX compounds (benzene, toluene, ethylbenzene and xylenes), as well as PAHs including benzo[a]pyrene, naphthalene and phenanthrene.

## 2.3 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a class of 209 chemical compounds referred to as congeners, in which between one and ten chlorine atoms are attached to a biphenyl molecule. The synthesis of PCBs was first reported in 1881, with full recognition of their industrial uses developing in the 1930s. The majority of PCBs were manufactured by the Monsanto Corporation between 1930 and 1977 for use in capacitors, transformers, printing inks, paints, pesticides and other applications. Monsanto marketed PCBs under the trade name Aroclor, distributing a variety of formulations differing from each other with respect to the amount and particular types of congeners present. Each Aroclor can be identified by a four-digit code. In most formulations, the first two digits in the code designate the number of carbon atoms in the biphenyl ring, while the last two digits designate the weight per cent chlorine. Aroclor 1254, for example, contains 12 carbon atoms in each biphenyl ring and 54 per

**Table 2** Composition (per cent) and selected properties of various Aroclors excluding carrier fluids (adapted from Cohen and Mercer, 1993)

| | Aroclor 1221 | Aroclor 1242 | Aroclor 1260 |
|---|---|---|---|
| **biphenyl** | 11.0 | – | – |
| **monochlorobiphenyl** | 51.0 | 1.0 | – |
| **dichlorobiphenyl** | 32.0 | 17.0 | – |
| **trichlorobiphenyl** | 4.0 | 40.0 | – |
| **tetrachlorobiphenyl** | 2.0 | 32.0 | – |
| **pentachlorobiphenyl** | 0.5 | 10.0 | 12.0 |
| **hexachlorobiphenyl** | – | 0.5 | 46.0 |
| **heptachlorobiphenyl** | – | – | 36.0 |
| **octachlorobiphenyl** | – | – | 6.0 |
| **Density ($kg/m^3$)** | 1180 | 1380 | 1560 |
| **Total (aqueous) solubility (µg/l)** | 200 | 240 | 2.7 |
| **Vapour pressure (Pa @ 25˚C)** | 0.893 | 0.053 | $5.333 \times 10^{-3}$ |
| **Viscosity (cP)** | 5 | 24 | resin |

cent chlorine by weight. Worldwide production of PCBs has now ceased, mainly in response to recognition of their toxicity and their tendency to bioaccumulate in animal tissues. However, they remain in limited use and may be present as impurities in locations where they were used previously.

PCBs were often blended with carrier fluids such as chlorobenzenes and mineral oil before distribution. Depending on the particular combination of congeners present and the type of carrier fluid, the density of most PCB oils encountered in practice ranges from approximately 1,100 to 1,500 kg/ m $^3$, while the viscosity ranges from approximately 10 to 50 cP. The relatively high density of PCB oils indicates that the timescale of migration may be relatively short, but their relatively high viscosity results in an intermediate range of timescales of migration. This means that PCB DNAPLs may still be migrating at some sites where they were introduced into the subsurface in the past few decades. As discussed, in largely on the viscosity and density of the DNAPL, together with a variety of other, site-specific factors.

With respect to impact on groundwater, most congeners are extremely hydrophobic and therefore sorb strongly onto soils and rock. Consequently, if PCBs are detected in groundwater samples, the DNAPL source is typically immediately up-gradient of the monitoring location. Exceptions are sites where colloid-facilitated transport is occurring or where the PCBs are dissolved in other organic contaminants such as oils. Carrier organic liquids may be LNAPLs as well as DNAPLs. PCB DNAPLs are often encountered at former solvent and waste oil recycling facilities where they have been co-disposed with a variety of other organic liquids such as chlorinated solvents and aromatic compounds. Table 2 presents the composition and selected physical properties of three particular Aroclors in the absence of any carrier fluids.

## 2.4 Chlorinated solvents

Chlorinated solvents such as trichloroethene (TCE), tetrachloroethene (PCE) and tetrachloromethane (carbon tetrachloride, CT, or CTET) form a class of DNAPL compounds that have been produced in large quantities throughout the world since the middle of the 20th century. Typical uses of these chemicals include dry cleaning, metal degreasing, pharmaceutical production, pesticide formulation and chemical intermediates. Chlorinated solvents typically enter the subsurface as a result of past disposal directly onto land, storage and disposal into unlined evaporation ponds and lagoons, leaking storage tanks and vapour degreasers, leaking piping and accidental spills during handling and transportation. Chlorinated solvents can be encountered as single component DNAPLs (for example, as primarily PCE at a dry-cleaning facility or as primarily TCE at a metal degreasing facility), or as part of a multi-component DNAPL containing other organic compounds such as PCB oils, mineral oils and fuels (for example, at a former solvent or waste oil recycling facility). Table 3 lists industries and industrial processes that have been associated historically with the presence of chlorinated solvent DNAPL in the subsurface.

**Table 3** Industries and industrial processes associated with chlorinated solvents

| Industry | Industrial process |
|---|---|
| **Electronics manufacturing** | Metal cleaning |
| **Solvent production** | Metal machining |
| **Pesticide/herbicide manufacturing** | Tool and die operations |
| **Dry cleaning** | Vapour and liquid degreasers |
| **Instrument manufacturing** | Paint stripping |
| **Solvent recycling** | Storage and transfer of solvents |
| **Engine manufacturing** | |
| **Steel product manufacturing** | |
| **Chemical production** | |
| **Rocket engine/ fuel manufacturing** | |
| **Aircraft cleaning/ engine degreasing** | |

The density of most chlorinated solvent DNAPLs ranges from approximately 1,100 to 1,600 kg/ m $^3$ and their viscosity from approximately 0.57 to 1.0 cP. Chlorinated solvent DNAPLs are therefore denser than water and typically less viscous than water.
This can result in rapid rates of subsurface migration and means that chlorinated solvent DNAPLs are typically no longer moving at sites where they were introduced to the subsurface even as recently as two or three years ago. Table 4 lists selected physical and chemical properties of commonly encountered chlorinated solvents. As can be seen, these compounds are volatile, indicating that they will give rise to vapour phase contamination in unsaturated media.

These compounds are typically characterised by low $K_{oc}$ values, indicating that aqueous phase plumes will not be strongly retarded relative to the rate of groundwater flow. $K_{oc}$ describes the distribution of an organic compound between water and the organic carbon content of the solid phase. High $K_{oc}$ values are characteristic of strongly sorbed compounds. Such compounds are significantly retarded with respect to groundwater flow. The relatively rapid rate of chlorinated solvent DNAPL migration and the relatively low degree of sorption are the two primary factors that distinguish this class of DNAPLs from creosote, coal tar and PCBs.

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**Table 4** Physical and chemical properties of selected chlorinated solvents (from Mackay *et al.*, 1993)

| Solvent | Molecular weight | Aqueous solubility (mg/l) | Density (kg/m$^3$) | Vapour pressure (Pa@˚C) | Viscosity (cP) | $K_{oc}$ (l/kg) |
|---|---|---|---|---|---|---|
| **trichloroethene** | 131.4 | 1,100 | 1460 | 9,000 | 0.57 | 126 |
| **tetrachloroethene** | 165.8 | 200 | 1620 | 2,600 | 0.90 | 364 |
| **tetrachloromethane** | 153.8 | 790 | 1590 | 15,000 | 0.97 | 439 |
| **trichloromethane** | 119.4 | 8,000 | 1480 | 26,000 | 0.56 | 44 |
| **chlorobenzene** | 112.6 | 500 | 1110 | 1,580 | 0.80 | 330 |
| **1,1,1-trichloroethane** | 133.4 | 1,320 | 1330 | 16,000 | 0.84 | 152 |

## 2.5 Mixed DNAPLs

In general, a DNAPL that is composed of only one chemical compound is referred to as a single component DNAPL. Dry cleaning fluid (typically tetrachloroethene) is an example of this (although, strictly, it too contains low concentrations of stabilisers and preservatives).
A DNAPL that is composed of two or more chemical compounds is referred to as a multi-component DNAPL. Creosote and coal tar are examples of multi-component DNAPLs. Whether a single component or a multi-component DNAPL exists at a site depends on past uses of the various compounds at the site and the methods of disposal. Table 5 presents the composition of a multi-component DNAPL obtained from a monitoring well at a former solvent recycling facility. Activities at this site resulted in the blending of various organic liquids prior to disposal.

As seen in **Table 5**, the DNAPL at this site contains chlorinated solvents, PCBs and a variety of aromatic compounds. Each of these components is available to dissolve from the DNAPL into groundwater.
The density of this particular DNAPL sample was measured as 1,200 kg/ m$^3$. It is interesting to note that the DNAPL contains toluene and xylenes, which are themselves less dense than water, but have combined here with heavier-than-water components to form a DNAPL.

The physical/chemical properties of the DNAPL may be spatially variable at a site. Seven DNAPL samples were obtained from this solvent recycling facility; each sample had different physicochemical properties, including the component composition.
The degree of spatial variability that may exist at a site with respect to the physicochemical properties of the DNAPL will depend on the site's use and history. Clearly, a solvent recycling facility with a long period of operation may exhibit significant spatial variability of DNAPL properties in the subsurface, while a small metal degreasing operation with a limited period of operation may result in a more uniform DNAPL composition.

Regardless of site history, however, DNAPLs encountered in the subsurface may have different physical and chemical properties from reagent grade non-aqueous phase liquids (NAPLs). This may be the result of industrial processes in which they were used prior to disposal or as a result of contact with naturally occurring substances present in the soil zone.

**Table 5** Component composition of DNAPL sample obtained from a solvent recycling facility

| Compound | Percentage mass |
|---|---|
| 1,1,1-TCA | 0.7 |
| TCE | 3.7 |
| PCE | 14.3 |
| toluene | 4.7 |
| m-xylene | 0.3 |
| o,p-xylene | 2.3 |
| 1,2,4-TCB | 0.10 |
| PCB-1242 | 40.6 |
| PCB-1254 | 7.1 |
| Petroleum hydrocarbons >C7 | 26.2 |

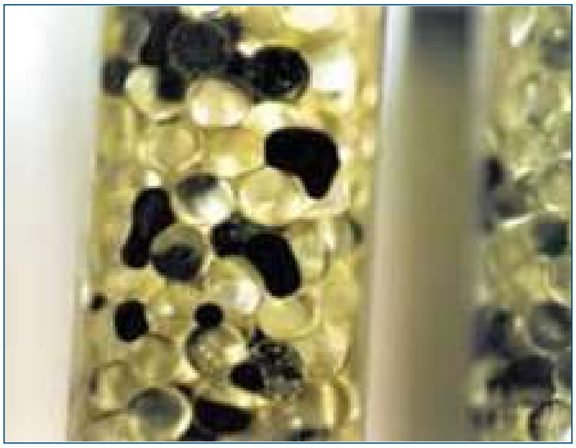

**Figure 1** Field DNAPL penetration into synthetic porous media

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