DNAPL Transport and Fate in the Subsurface

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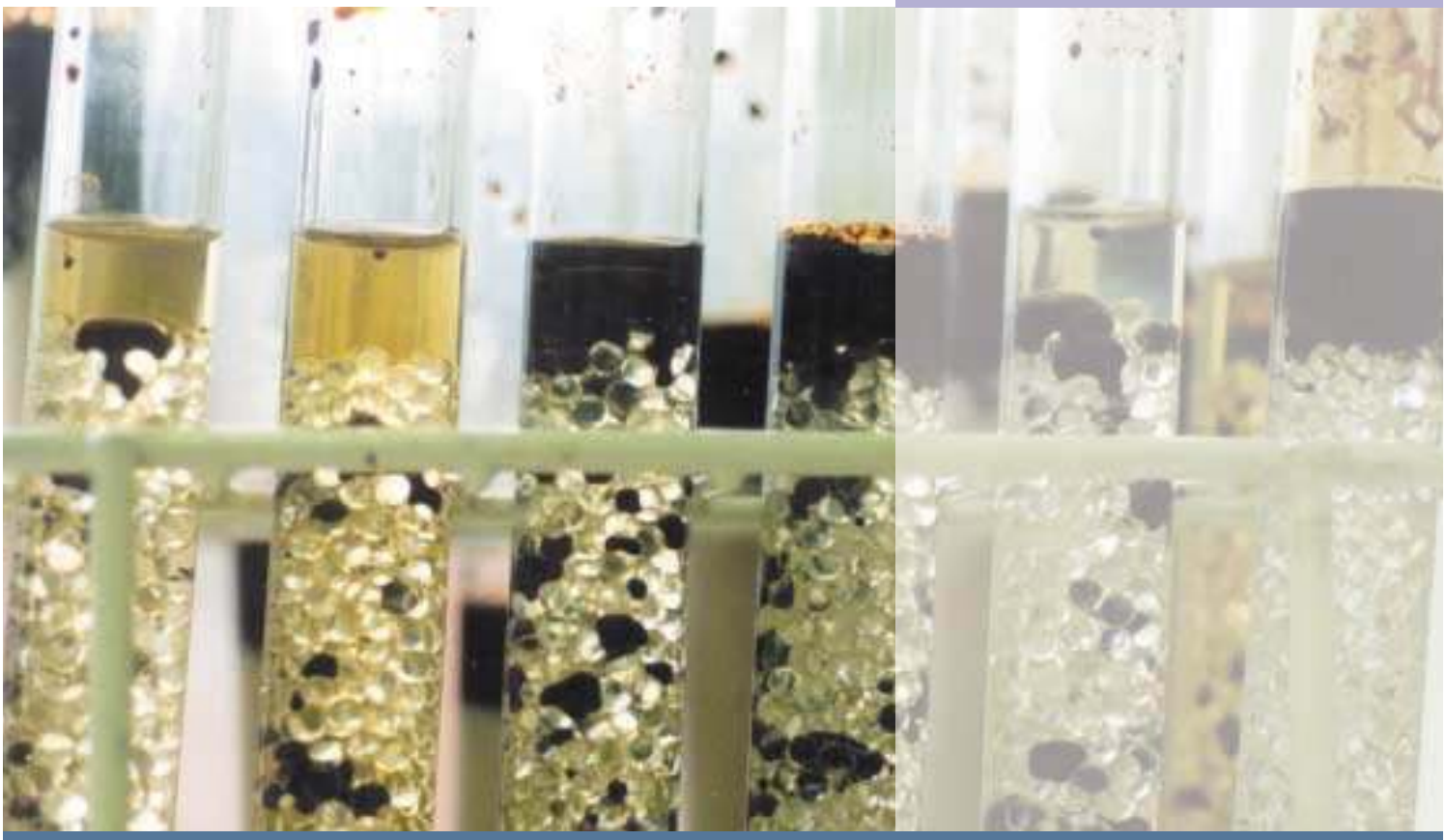

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An illustrated handbook of DNAPL transport and fate in the subsurface

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Coal tar DNAPL penetrating synthetic porous medium of glass beads. Courtesy of Prof S.Leharne, University of Greenwich.

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Statement of use:
This report describes current understanding of DNAPL fate and transport in the subsurface. It applies those concepts to hydrogeological conditions found in the UK, in order to develop a series of conceptual models of DNAPL behaviour following its release into the subsurface environment. It will help practitioners understand the principles of DNAPL fate and transport in the subsurface, and allow improved design of investigation and assessment of DNAPL pollution.

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Environment Agency R&D Publication 133

Executive summary

Dense non-aqueous phase liquids (DNAPLs) such as creosote, coal tar, chlorinated solvents and polychlorinated biphenyl oils represent a particular class of soil and groundwater contaminant that exist as a separate liquid phase in the presence of water. DNAPLs come to rest in the subsurface as disconnected blobs and ganglia of liquid referred to as residual DNAPL, and in potentially mobile distributions referred to as pools.

The region of the subsurface containing residual and pooled DNAPL is referred to as the source zone. Groundwater flowing through the source zone slowly dissolves the DNAPL, giving rise to aqueous phase plumes of contamination hydraulically down-gradient of the source zone. Some DNAPL compounds are resistant to biodegradation and sorb little; they can therefore give rise to substantial aqueous phase plumes. Other DNAPL compounds are relatively immobile in groundwater and, therefore, are highly retarded relative to the rate of groundwater flow. In unsaturated media, volatile DNAPLs give rise to vapour phase contamination.

Because DNAPLs are only slightly soluble in water, DNAPL source zones can persist for many decades and, in some cases, even hundreds of years. Some DNAPLs are highly toxic and even very low concentrations in groundwater or the atmosphere can pose an unacceptable risk to human health or the environment.

The fact that DNAPLs are denser than water allows them to migrate to substantial depths below the water table in both unconsolidated deposits and fractured bedrock. Delineating the spatial extent of the DNAPL source zone at a site can be a substantial undertaking, requiring at times several years of investigation and significant financial resources.

Remediation strategies are site-specific, with separate approaches often warranted for the DNAPL source zone and its associated aqueous phase plume. There has been limited success in removing all DNAPL from below the water table at sites, particularly in a fractured rock environment. Remediation strategies are therefore often directed towards source zone containment or stabilisation, partial mass removal, plume management or plume interception, within the framework of appropriate risk-management objectives.

The purpose of this handbook 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, conducting risk assessments and selecting remediation approaches. While this handbook 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' compared with many other areas of science and engineering. Readers are therefore advised to keep abreast of the new advances in understanding and approaches expected in the foreseeable future.

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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 hydrogeologicalz 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 handbook 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 handbook 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. The reader is therefore advised to keep abreast of the new advances in understanding and approaches expected in the foreseeable future.

2

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 handbook; 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	

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	5.333×10^{-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.

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

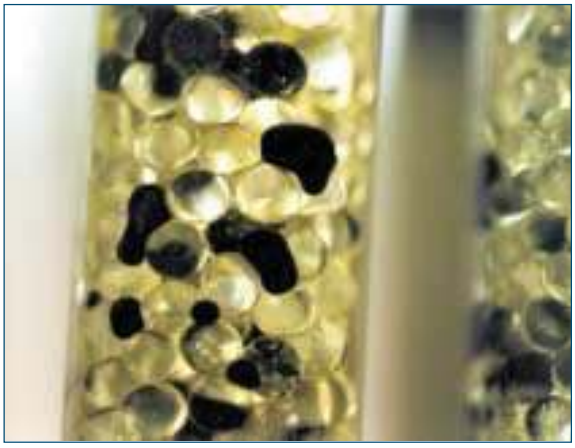


Figure 1 | Field DNAPL penetration into synthetic porous media

DNAPL Source zones in unconsolidated deposits

Upon release at the ground surface, the DNAPL will migrate both vertically and laterally in the subsurface (**Figure 2**). Residual DNAPL, in the form of disconnected blobs and ganglia of organic liquid,is formed at the trailing end of a migrating DNAPL body. The formation of residual DNAPL, which occurs in response to pore-scale hydrodynamic instabilities, always takes place. The individual blobs and ganglia of organic liquid comprising residual DNAPL are typically between 1 and 10 grain diameteres in length. Residual DNAPL will form in both unsaturated and saturated media, and is held in place by capillary forces that arise because the interface between the DNAPL and water, and the interface between DNAPL and air, is in a state of tension.

The amount of residual DNAPL retained by a typical porous medium such as silt, sand and gravel is typically between 5 and 20 per cent of the pore space in the particular lenses and laminations invaded by the DNAPL.

Figure 3(b) presents a close-up view of residual DNAPL in saturated porous media. The residual DNAPL forms discrete blobs and ganglia of liquid that are disconnected from each other. In most types of porous media, even relatively large hydraulic gradients cannot mobilise residual DNAPL. Site investigation activities such as pumping tests and well purging will therefore not draw residual DNAPL into well screens and sand packs.

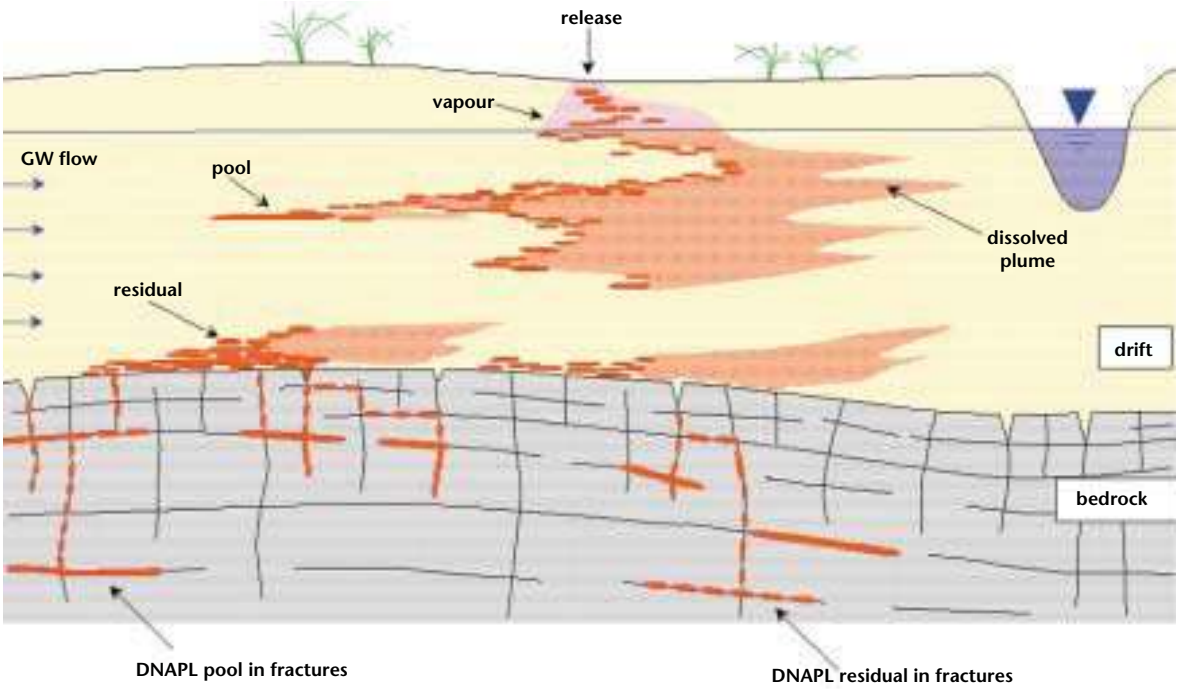


Figure 2 | DNAPL distribution in unconsolidated deposits (after Pankow and Cherry, 1996)

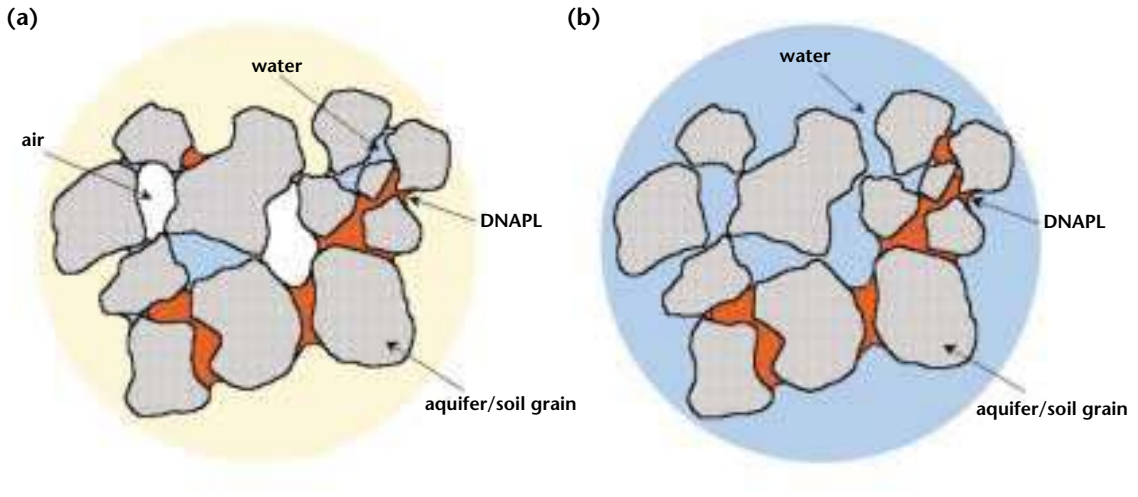


Figure 3 | Residual DNAPL in (a) unsaturated and (b) saturated porous media

The various blobs and ganglia of residual DNAPL dissolve slowly into flowing groundwater, giving rise to aqueous phase plumes. Because the solubility of most DNAPLs is relatively low in water and groundwater velocities are typically low, it can be many decades before all residual DNAPL is depleted due to natural processes.

Figure 3(a) presents a close-up view of residual DNAPL in unsaturated porous media. As in saturated porous media, the DNAPL forms discrete blobs and ganglia of liquid that are disconnected from each other. The DNAPL blobs are exposed to both air and water, allowing for both vapourisation into the air phase across DNAPL-air interfaces and dissolution into infiltrating water across DNAPL-water interfaces. Once present in soil moisture, dissolved contaminants will be available for partitioning across air-water interfaces (a process referred to as volatilisation).

Because the vapour pressure of many DNAPL compounds is relatively high, the lifespan of residual DNAPL in the unsaturated zone can be much less than the lifespan of residual DNAPL below the water table. The vapourisation process can deplete residual chlorinated solvent DNAPLs such as TCE and PCE within 5-10 years in relatively warm and dry climates. This will not eliminate the presence of vapour phase, absorbed phase and aqueous phase contamination in the unsaturated zone, but it can lead to an absence of the DNAPL phase. The absence of chlorinated solvent DNAPL in the unsaturated zone at a site should not, in general, be used as a basis for concluding that past releases of DNAPL did not occur at that site or that past releases of DNAPL failed to reach the water table.

As illustrated in **Figure 2**, DNAPL in unconsolidated deposits can also come to rest in larger accumulations referred to as pools. DNAPL pools tend to form above finer grained horizons that provide the necessary capillary resistance to support the DNAPL accumulation. Unlike residual DNAPL, pools contain DNAPL that is continuous between adjacent pores, with local saturations of up to approximately 70 per cent of the pore space. The finer grained horizon upon which DNAPL pooling can occur need not be a well-defined, laterally extensive clay unit. DNAPL pooling can occur on silt and fine sand horizons at all elevations within unconsolidated deposits. The maximum pool height is inversely proportional to the permeability of the particular horizon upon which pooling is taking place, with clay and silt units typically supporting higher pools than fine sand horizons.

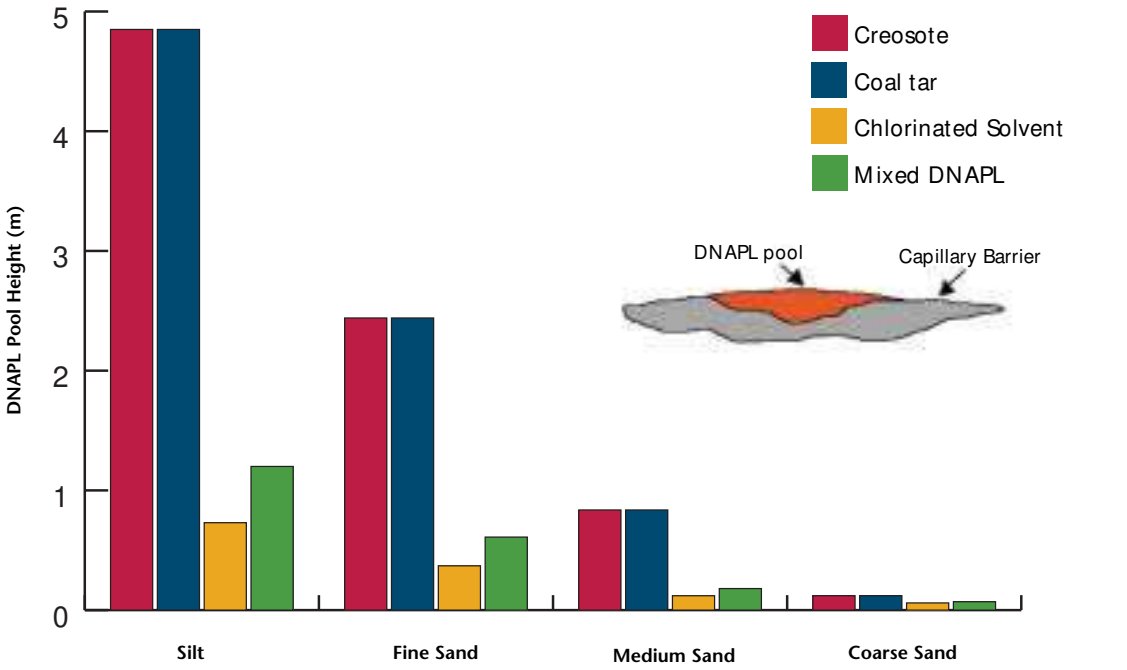


Figure 4 | Maximum DNAPL pool height above various capillary barriers

Figure 4 illustrates typical maximum pool heights for coal tar, creosote, a chlorinated solvent and a mixed DNAPL perched above a variety of capillary barriers. The calculations and assumptions adopted in **Figure 4** are outlined in Appendix A. Larger pool heights can form for higher DNAPL-water interfacial tension, lower DNAPL density and lower capillary barrier permeability. For chlorinated solvent and PCB DNAPLs, pool heights typically range from a few centimetres to several tens of centimetres. Chlorinated solvent pools as thick as 2m have been reported at sites in the USA, but this is a relatively rare occurrence. For creosote and coal tar, DNAPL pool heights are generally larger than those associated with PCB and chlorinated solvent DNAPLs because of the lower density of these compounds.

Unlike residual DNAPL, pooled DNAPL is relatively easy to mobilise with increases in the hydraulic gradient (this is the basis for water flooding to enhance crude oil recovery in the oil industry). Unless the risk of vertical DNAPL mobilisation is acceptable, care must be taken to avoid performing pumping tests beneath DNAPL source zones. Drilling through pooled DNAPL also carries with it a risk of vertical DNAPL mobilisation and many practitioners adopt an 'outside-in' approach to delineating DNAPL sites in order to minimise the chances of directly encountering pooled DNAPL during site characterisation.

Residual and pooled DNAPL collectively form what is referred to as the DNAPL source zone. It is within the DNAPL source zone that dissolution into groundwater occurs and aqueous phase plumes originate. DNAPL will not migrate downwards through unconsolidated media as a uniform body, but instead will migrate along multiple pathways in a very tortuous manner; this is sometimes referred to as dendritic form due it its resemblance to the branches of a tree.
The specific migration pathways will be governed by the bedding structure of the porous medium, with migration occurring along pathways on the scale of millimetres to metres. In horizontally bedded media, significant amounts of lateral spreading can be expected, including in directions not coincident with the direction of groundwater flow. The field experiments reported by Poulsen and Kueper (1992), and Kueper *et al.* (1993) demonstrated, for example, that the orientation of bedding structures (**Figure 5**) is the primary factor controlling the directions and specific pathways of DNAPL migration, which can be seen red due to SUDAN IV dye.

These experiments also demonstrated that slow, dripping releases of DNAPL are likely to migrate to greater depths than sudden, single event releases. It is therefore not practicable to define all of the specific DNAPL migration pathways at a typical industrial site.

A much more attainable, yet still difficult, goal is to define the lateral extent of the DNAPL source zone, without specific delineation of residual DNAPL and DNAPL pools within the overall source zone.

Given the selective and tortuous nature of DNAPL migration, it follows that the majority of porous media within a DNAPL source zone will contain neither residual nor pooled DNAPL. The probability of directly encountering residual or pooled DNAPL with a conventional drilling programme is therefore relatively small. It is now commonly accepted that direct visual observation of DNAPL does not occur at most DNAPL sites. Instead (as discussed in Section 7), the presence of DNAPL is inferred using alternative lines of evidence. The overall bulk retention capacity of porous media within a DNAPL source zone is generally thought to range from approximately 0.5 to 3 per cent. This retention capacity is defined as the volume of DNAPL (as both residual DNAPL and pools) divided by the overall bulk volume of the source zone. These values are lower than local-scale residual saturations (5-20 per cent of the pore space) because they are expressed in relation to the bulk volume impacted and because not all lenses and laminations within the impacted zone will have been invaded by the DNAPL. Exceptions will occur at some sites, with some source zones containing bedding structures and capillary properties capable of retaining higher amounts.

Lower DNAPL density, higher DNAPL viscosity, and higher DNAPL-water interfacial tension generally lead to larger amounts of lateral DNAPL spreading both above and below the water table. Creosote, for example, has been observed to have migrated hundreds of metres from release locations at certain sites in the USA. The extent of lateral migration of chlorinated solvent DNAPLs tends to be less, but has been observed to be tens to hundreds of metres at many sites. This had led to a useful rule of thumb that in horizontally bedded media, 'DNAPL must migrate sideways in order to migrate down'.

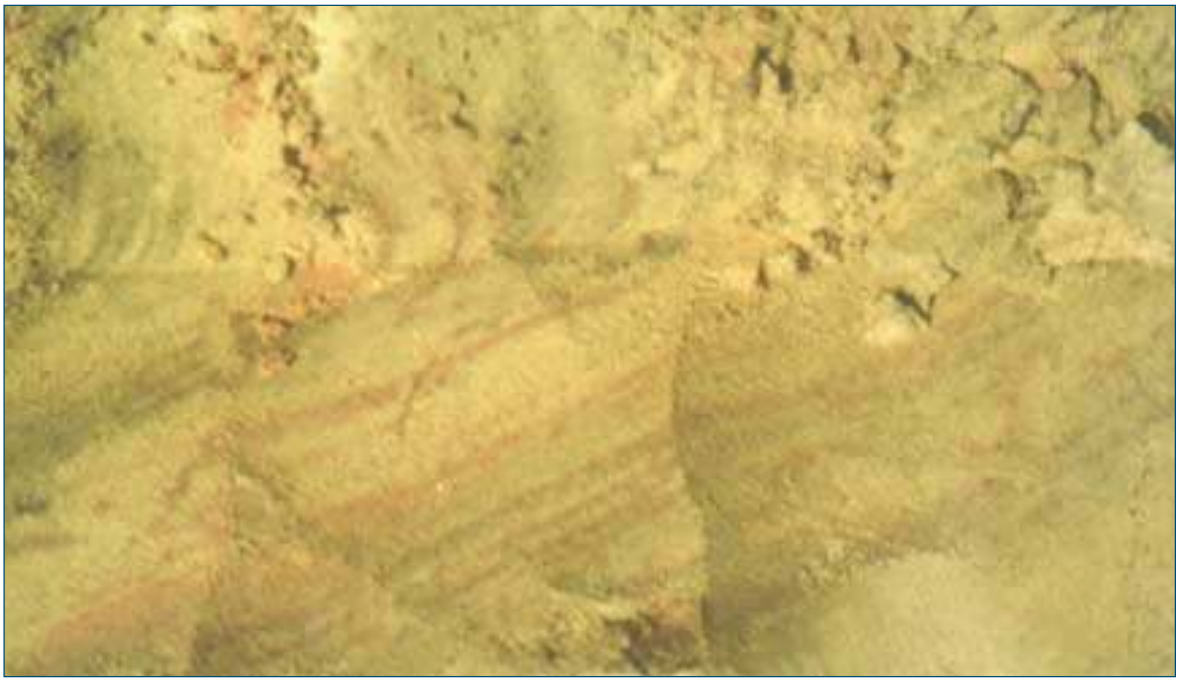


Figure 5 DNAPL migration pathways in unsaturated sands. DNAPL presence shows red due to SUDAN IV dye. Bedding dips 30° below horizontal (source: Poulsen and Kueper, 1992). Image is 15 cm from top to base

DNAPL dissolution in unconsolidated deposits

Both residual DNAPL and pools will dissolve into groundwater flowing through the DNAPL source zone, giving rise to aqueous phase plumes. Given the tortuous and sporadic nature of DNAPL occurrence within the source zone, it follows that the associated aqueous phase plumes will exhibit significant spatial variability in terms of concentration.

Figure 6a illustrates a vertical cross-section through a DNAPL source zone along with a depiction of the associated aqueous phase plumes. Monitoring wells have been placed at various locations in the cross-section, along with posted concentrations. **Figure 6b** shows the possible result if the posted concentrations are contoured; it gives the impression of a single, smoothly varying distribution of concentrations but this is an over-simplification of the true spatial distribution of concentrations. Although discrete sampling devices are commercially available to profile groundwater plumes at the scale of centimetres, this level of detail is usually not required (or achieved) in site investigations.

Various factors influence the magnitude of contaminant concentrations obtained from monitoring well samples relative to the actual concentrations in the aquifer. **Figure 7** depicts a single monitoring borehole downstream of a zone of residual DNAPL. For the purposes of this discussion, it is assumed that the DNAPL is TCE, with an aqueous solubility of 1,100 mg/l. At point A (immediately down-gradient of the zone of residual DNAPL), one would expect the local

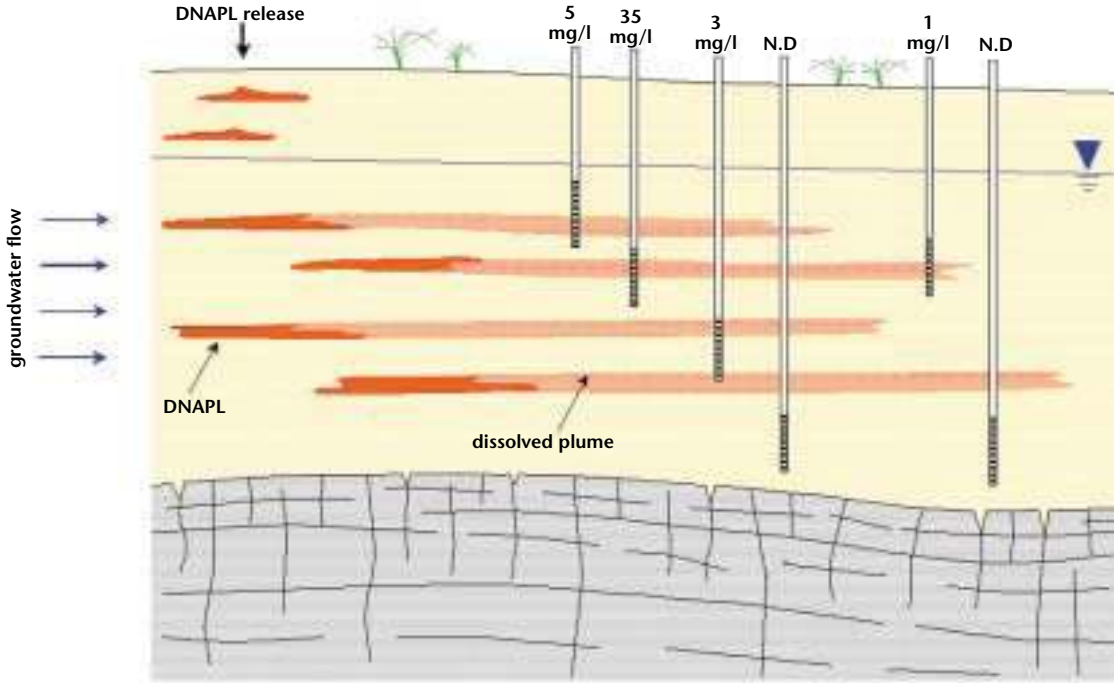


Figure 6a | Cross-section depicting spatial variability of groundwater concentrations in a plume

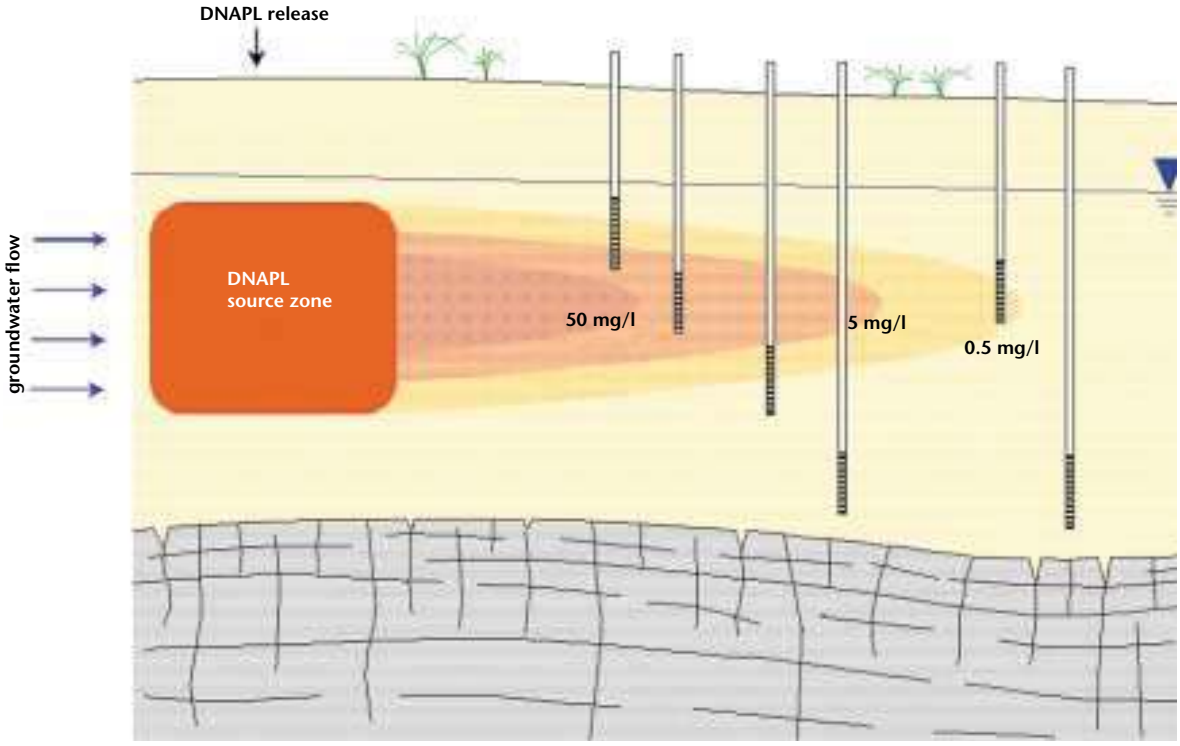


Figure 6b Visual appearance of a smoothly varying distribution of concentration following contouring

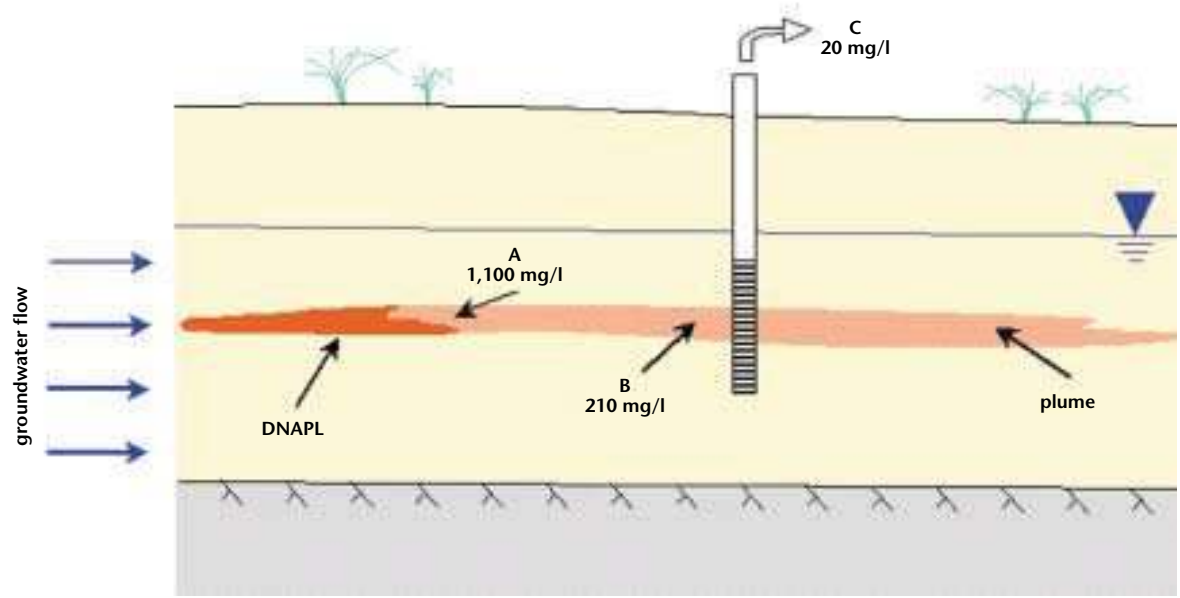


Figure 7 Visual appearance of a smoothly varying distribution of concentration following contouring

groundwater concentration to be approximately 1,100 mg/l. As we move downstream to point B, the concentration will be less due to hydrodynamic dispersion. Dispersion always occurs in the subsurface and results in a lowering of concentrations along the centreline of a plume in the downstream direction. The maximum concentration of 1,100 mg/l can only be observed immediately adjacent to the DNAPL and will not be observed anywhere down-gradient of the source zone.

Point C represents a groundwater sample obtained from the monitoring borehole after water has been purged from the borehole. The concentration in the groundwater sample is significantly less than that at point B due to in-borehole dilution. This refers to the fact that pumping the monitoring borehole draws in both the local contaminant plume as well as surrounding uncontaminated water. The result is a mixing of clean and contaminated water in the monitoring well, and a resulting lowering of concentrations in the obtained sample relative to what may be present in the aquifer immediately adjacent to the well. In addition to mixing during purging, this in-borehole dilution effect can occur naturally if vertical flow gradients exist within the borehole.

It was assumed in the above example that the monitoring well of interest was placed precisely along the centre line of the plume, where maximum contaminant concentrations will exist. If the monitoring well were placed offset from the plume centre line, sampled concentrations would be even lower. This is because contaminant concentrations decrease in the transverse direction (both horizontally and vertically) away from the plume centre line. In addition to monitoring well placement and the factors discussed above, biotic and abiotic degradation can result in the lowering of concentrations in the down-gradient direction within a contaminant plume.

The net effect of hydrodynamic dispersion, in-borehole dilution, monitoring well placement and potential degradation processes is that contaminant concentrations in a sample obtained from a monitoring well downstream of a DNAPL source zone may be significantly less than the aqueous solubility of the DNAPL of interest. Experience has shown that a DNAPL source may be present upstream of a monitoring well if sample concentrations exceed 1 per cent of the effective solubility of the component of interest (US EPA, 1992). The 1 per cent 'rule of thumb' has been criticised because it does not provide guidance on how far upstream the DNAPL source zone is located. It is clear that a variety of site-specific factors influence the magnitude of sampled contaminant concentrations and that some of these factors cannot be determined (for example, the distance a monitoring well is offset from plume centre line and the amount of in-borehole dilution occurring during purging). In practice, it is common to simply use the 1 per cent 'rule of thumb' as a means of establishing that DNAPL may be present upstream of the monitoring well in question, and therefore as a means of justifying the use of additional site investigation techniques to confirm or refute the presence of DNAPL. In other words, the 1 per cent 'rule of thumb' should not be used in isolation to establish DNAPL presence at a site, but instead should be used with other converging lines of evidence to both establish DNAPL presence and to delineate the spatial extent of the source zone. Site techniques to establish DNAPL presence and delineate the spatial extent of the source zone are discussed in Section 7.

The above discussion assumed that the DNAPL of interest was composed only of TCE. If the DNAPL of interest is composed of a variety of components, these components will not dissolve into groundwater at their single component, textbook solubility values. Rather, the various components may compete for the dissolution process. The dissolution of a multi-component NAPL can be described using Raoult's law. Raoult's law states that the effective solubility of a NAPL component in (ground)water is equal to the product of the mole fraction in the NAPL and the single component aqueous solubility of that compound:

Equation 1

$$C_i = m_i S_i$$

where:

C_i is the effective solubility of component i;

m_i is the mole fraction of component i in the NAPL;

S_i is the single component solubility of component i.

In practical terms, the effective solubility of a component is the maximum concentration that could possibly be observed in groundwater. Sample concentrations obtained from monitoring wells in the plume will be less than the effective solubility due to in-borehole dilution, hydrodynamic dispersion and other effects. The relative concentration of individual components, however, is dictated by Raoult's law. In terms of the 1 per cent 'rule of thumb', it is 1 per cent of the effective solubility that is taken as an indicator of possible upstream DNAPL presence, not 1 per cent of the single component solubility.

To illustrate the effects of Raoult's law, consider a three-component DNAPL consisting of 50 per cent chloromethane (methylene chloride), 25 per cent toluene and 25 per cent of a semi-volatile organic compound (SVOC) by mass. Chloromethane has a relative molecular mass of 84.93, a density of 1,327 kg/m^3 and a single component aqueous solubility of 20,000 mg/l. Toluene has a relative molecular mass of 92.1, a density of 867 kg/m^3 and a single component aqueous solubility of 500 mg/l. The SVOC is assigned a relative molecular mass of 200, a density of 1,100 kg/m^3 and a single component aqueous solubility of 10 mg/l. Toluene represents the intermediate molecular weight and intermediate solubility component, while chloromethane represents the most soluble and lowest molecular weight component. In this example, the DNAPL is assumed to be present at a residual saturation of 20 per cent in a 1 m^3 volume of fine-grained sand having a hydraulic conductivity of 1 x 10^{-5} m/s, a porosity of 0.30, and to be subject to a hydraulic gradient of 0.01. The DNAPL is assumed to be dissolving into groundwater under equilibrium conditions according to Raoult's law.

Figure 8 presents the aqueous concentrations of the three compounds of interest exiting the 1 m^3 of aquifer material as a function of time. **Figure 8** shows that the chloromethane concentration declines with time, while the toluene and SVOC concentrations display moderate increases. The rapid decline of the chloromethane concentration stems from the fact that it has the highest effective solubility (C_i) according to Raoult's law. As the chloromethane is preferentially depleted from the NAPL at an early time, the NAPL becomes enriched in the lower effective solubility compounds, which then show corresponding increases in their effective solubilities. In addition, the total concentration (sum of the three compounds) decreases with time. This illustrates that a decrease in total concentration with time does not indicate that DNAPL is not present; it is simply a result of the fact that the higher solubility compounds are preferentially depleted from the DNAPL at an early time.

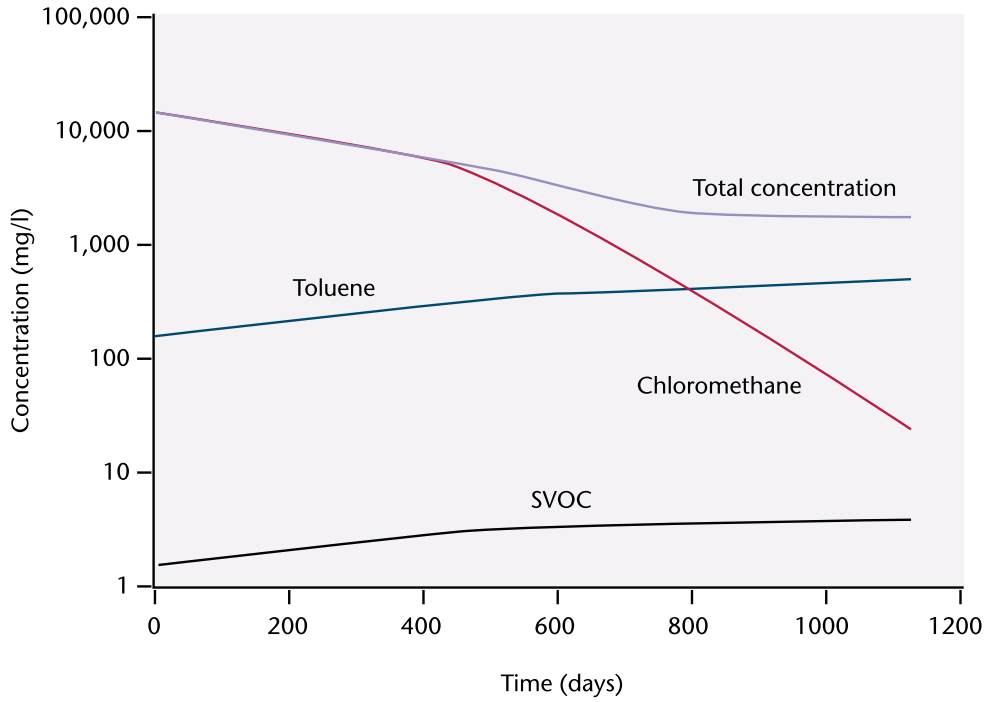


Figure 8 Aqueous phase concentrations immediately downstream of DNAPL source

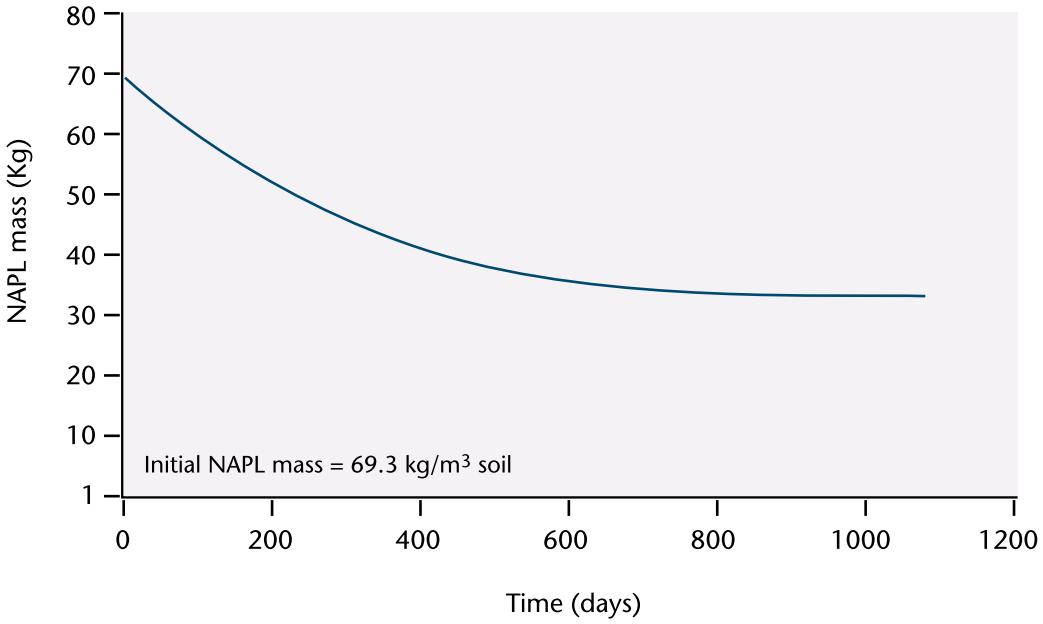


Figure 9 | DNAPL mass versus time

Figure 9 presents a plot of DNAPL mass in the 1 m^3 of aquifer material as a function of time. At $t = 0$, 69.3 kg of DNAPL is present in the sample volume. The DNAPL mass decreases with time as the three components dissolve into flowing groundwater, but the rate of mass depletion slows appreciably after approximately 400 days once most of the chloromethane has been depleted. The slower rate of mass depletion with increasing time is consistent with the fact that the total concentration (**Figure 8**) decreases with time.

This example illustrates some fundamental aspects of multi-component DNAPL dissolution applicable to all sites. In summary, the dissolution of a multi-component DNAPL into groundwater will be characterised by the preferential depletion of the higher effective solubility components at an early time. These components will therefore display decreasing concentrations with time. The lower effective solubility components will display slower rates of concentration decrease with time, with some components displaying moderate increases in concentration with time. The total concentration of all components will decrease with time. This should not be mistaken as an indication that DNAPL is not present. In addition, DNAPL mass will decrease fastest at an early time (after DNAPL entry), showing increasingly slower rates of mass depletion as time progresses from the initial entry of DNAPL into the groundwater.

Raoult's law is based on the premise that the various components compete for the dissolution process. However, if the DNAPL of interest contains a co-solvent such as a low molecular weight alcohol, the presence of the co-solvent may invalidate the use of Raoult's law and result in an enhancement of the various component solubilities in groundwater. This co-solvent effect typically only occurs for relatively high co-solvent concentrations (for example, 20 per cent co-solvent or more by mass in the DNAPL) and tends to be relatively short-lived (the co-solvent will deplete itself quickly from the DNAPL at an early time).

DNAPL source zones in fractured rock

DNAPL will enter fractures in bedrock both above and below the water table. Analogous to unconsolidated deposits, both residual DNAPL and pools will form in rock fractures, with a higher likelihood of pool formation in horizontal to sub-horizontal features. Fracture entry pressures are directly proportional to interfacial tension and inversely proportional to fracture aperture. This results in preferential DNAPL migration through the larger aperture fractures of a fracture network. The strike and dip of the more permeable fractures will therefore control the primary directions of DNAPL migration in a fracture network. **Figure 2** (see Section 3) illustrates the presence of DNAPL in fractured rock below the water table; note that not all fractures of the network have been invaded and that substantial amounts of lateral DNAPL migration have taken place through horizontal features.

Once DNAPL enters a fracture network, it is probable that continued downward and lateral migration occurs until the source of DNAPL to the bedrock is exhausted. **Figure 10** illustrates a pool of DNAPL at the base of overburden overlying fractured bedrock. The depiction in **Figure 10** is unlikely in that the DNAPL has come to rest as a continuous vertical distribution between the pool in overburden and some depth denoted as point A. The depiction is unlikely because capillary pressure increases linearly with depth in a hydrostatic system; this means that the fracture aperture at point A would need to be extremely small to support the overlying distribution of DNAPL.

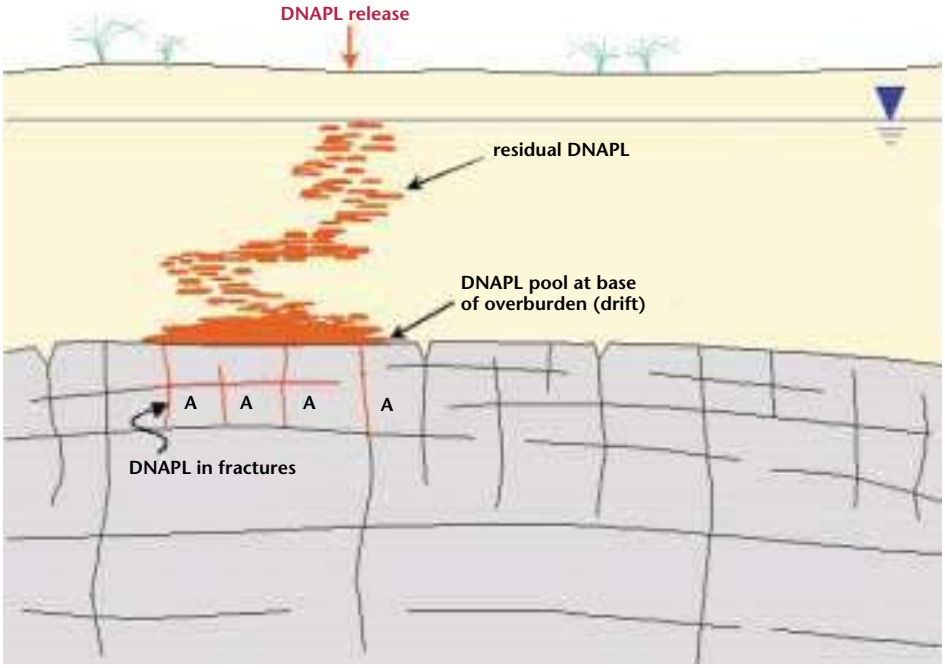


Figure 10 DNAPL pool at base of overburden: unlikely scenario

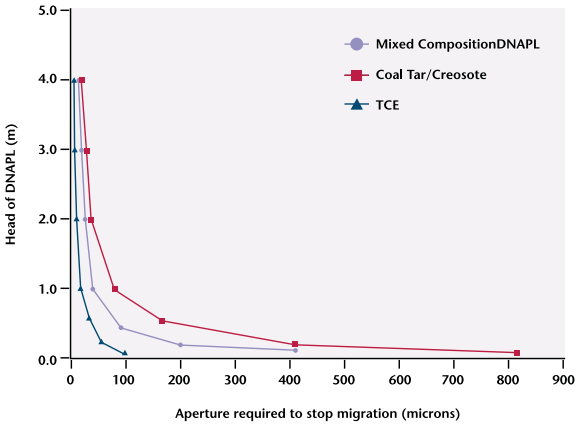


Figure 11 | Fracture aperture required to stop migration versus height of accumulated DNAPL

Figure 11 presents a plot of the fracture aperture required to stop migration versus depth for a variety of DNAPL types. Appendix B outlines the calculation procedure used to produce this graph. The fracture aperture required to stop migration denotes the largest aperture that can exist at the corresponding depth such that DNAPL migration is arrested, resulting in the depiction illustrated in **Figure 10**. For chlorinated solvents such as TCE, fracture apertures need to decrease quickly with depth in order to prevent further downward migration. **Figure 11** indicates that even a 1m accumulation of TCE in fractured rock would require apertures to be no larger than 9 µm at the base of the accumulation in order to prevent further downward migration. (By way of comparison, a human hair is approximately 50 µm thick). Experience has shown that fractures remain open to depths of many hundreds of metres in many rock types, with measured apertures in the order of hundreds of micrometres at many sites. **Figure 11** assumes that water is perfectly wetting with respect to the DNAPL of interest. If contact angles between the water and DNAPL were greater than zero degrees, even smaller fracture apertures would be required to arrest migration.

Figure 11 shows that less dense DNAPLs such as creosote and coal tar do not require as drastic a reduction in fracture aperture with depth to arrest downward migration, but that significant reductions are still required to support an accumulation of DNAPL. A head of creosote or coal tar of 2 m, for example, would require all fracture apertures below the DNAPL to be less than 41 µm to prevent downward migration. All the fractures are rough-walled and therefore exhibit a range of apertures within the fracture plane. In the above example, the largest aperture within the fracture plane needs to be restricted to 41 µm or less in order to arrest downward DNAPL migration.

Figure 12 presents the much more likely scenario in which DNAPL is only present as residual at the base of overburden, with a significant migration to depth in the fracture network. The absence of pooled DNAPL at the base of overburden is therefore not an indication that DNAPL has not entered fractured bedrock.

For chlorinated solvent DNAPLs with densities significantly greater than water and relatively low viscosities, it is probable that DNAPL migration to a considerable depth in the fracture network will have occurred, and that the DNAPL is no longer moving, by the time site investigations begin. For creosote and coal tar DNAPLs, however, which are characterised by lower densities and higher viscosities, migration in the fracture network may still be occurring today in response to releases that occurred many decades ago. In such cases, DNAPL at the shallower elevations may have reached a stable configuration of residual DNAPL and pools, but DNAPL at depth may still be migrating.

Given the fact that DNAPLs are likely to have migrated to considerable depth in bedrock systems, careful consideration must be given to drilling activities aimed at determining the total depth of migration. At most sites, the total depth of DNAPL migration in fractured bedrock is not determined. This stems from the fact that drilling through DNAPL source zones carries with it an associated risk of re-mobilising DNAPL, allowing it to migrate deeper into the subsurface. Because DNAPL does not enter all the fractures in a network, a large number of boreholes may be required to estimate the depth of DNAPL migration; such an exercise is often prohibited by cost. Furthermore, knowledge of the depth of migration is often of little practical use because remediation technologies are currently unable to remove DNAPL completely from depth in bedrock systems. The aqueous phase plume is typically the most mobile form of contamination. Drilling efforts are therefore often focused on determining the rate and direction of plume migration, with particular emphasis on data collection to assess the likely risks to identified receptors.

The overall ability of fractured bedrock to retain residual and pooled DNAPL is relatively small given the low fracture porosity of most rock types. A typical fractured rock, for example, may exhibit fracture porosities in the range of 0.001 to 0.01. Assuming that DNAPL will occupy on average 20 per cent of the fracture pore space, this range of fracture

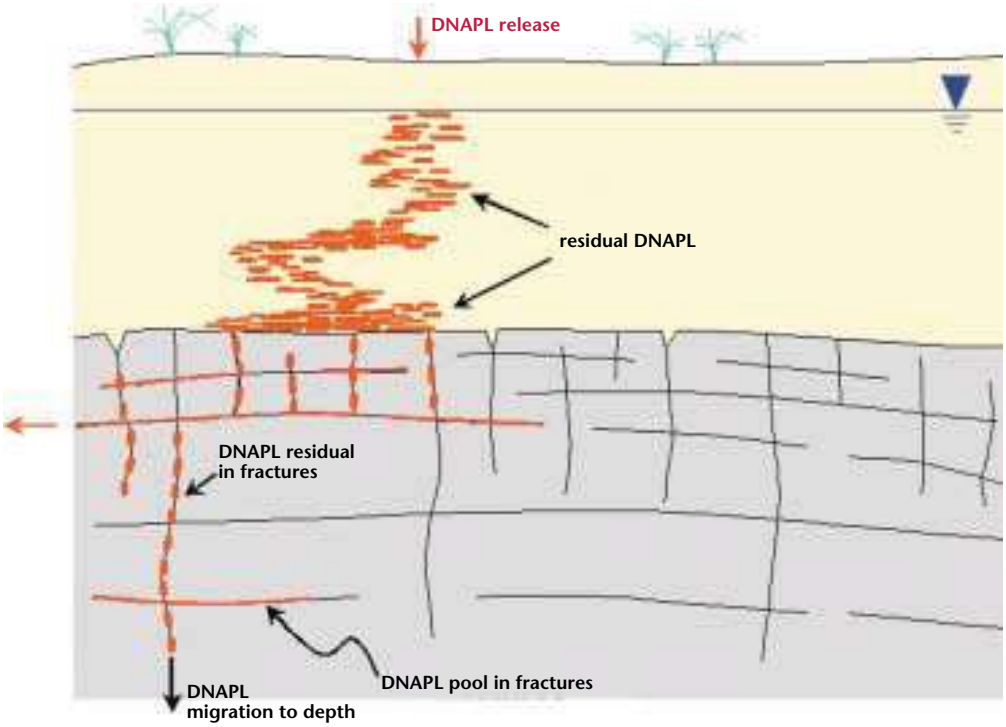


Figure 12 DNAPL migration to depth in fractured bedrock: likely scenario

porosities corresponds to bulk retention capacities ranging from 0.0002 m^3 DNAPL per m^3 of bedrock to 0.002 m^3/m^3 (that is, between 200 ml and 2 litres of DNAPL per m^3 of rock). This implies, for example, that one drum of DNAPL containing 205 litres (0.205 m^3) of product will occupy a bulk bedrock volume of 103-1,025 m^3.

It is clear that relatively small volumes of DNAPL have the potential to impact relatively large volumes of bedrock. This conclusion holds for most rock types in the UK, including all the major water supply aquifers. Drilling through an overburden DNAPL source zone into underlying bedrock should thus be approached with caution. Care should be taken to grout casings into competent rock before drilling deeper, and a DNAPL contingency plan to identify and recover DNAPL during drilling activities should be in place.

It should also be pointed out that downward groundwater flow can mobilise DNAPL pools deeper into the subsurface. The specific mechanism causing the mobilisation of DNAPL is a manipulation of capillary pressure in response to the imposed hydraulic gradient in the groundwater. Pumping tests in bedrock should therefore generally be avoided beneath overburden DNAPL source zones where a small amount of downward DNAPL mobilisation could bring about contamination of a large volume of bedrock. De-watering overburden deposits by lowering the water table into bedrock should also, in general, be avoided.

The discussion above has focused on the migration of DNAPL through bedrock fractures. In cases where the rock matrix is relatively coarse-grained, some entry of DNAPL into the rock matrix may also occur. This is generally not a concern in crystalline rocks, chalk and limestones, but may be a concern in the Triassic sandstones encountered in the UK where relatively coarse-grained sediments and small amounts of calcite/dolomite cement characterise the rock matrix. In cases where the DNAPL is wetting with respect to water (not common, but possible especially with coal tars), spontaneous imbibition of the DNAPL into the rock matrix can occur.

DNAPL dissolution in fractured rock

Once DNAPL is present in bedrock, it will slowly dissolve into groundwater flowing through open fractures, giving rise to aqueous phase plumes. The plumes will generally migrate in the hydraulically down-gradient direction subject to advection, dispersion, sorption to fracture walls, possible biodegradation and matrix diffusion. As with plume migration in unconsolidated deposits, the chemical composition of the plume will be a function of the chemical composition of the DNAPL. Therefore, the plume would expect to be dominated by higher effective solubility compounds at an early time, gradually shifting later towards higher concentrations of the lower solubility compounds. Like plumes in unconsolidated deposits, all plumes in fractured bedrock will eventually reach a steady-state configuration where the leading and side edges of the plume (as defined by a specific concentration level) are no longer expanding. One objective of many site investigations is to determine whether the aqueous phase plume has reached its steady-state configuration.

Figure 13 illustrates the development of a steady-state plume downstream of a DNAPL source zone that is providing a constant concentration source of contamination. The concept of a steady-state plume is applicable to both porous and fractured media, and can result from the dispersion process alone. As a result, all plumes reach a steady-state configuration at some point in time where the leading and side edges of the plume are stable as defined by a specified concentration contour and ultimately, once the source zone is exhausted, will shrink. **Figure 13** shows that the monitoring well closest to the DNAPL source zone reaches a steady-state concentration at time t_1 .The next monitoring well reaches a steady-state concentration at t_2, which is greater than t_1. The monitoring well near the leading edge of the plume reaches a steady-state concentration at t_3, which is greater than t_2.

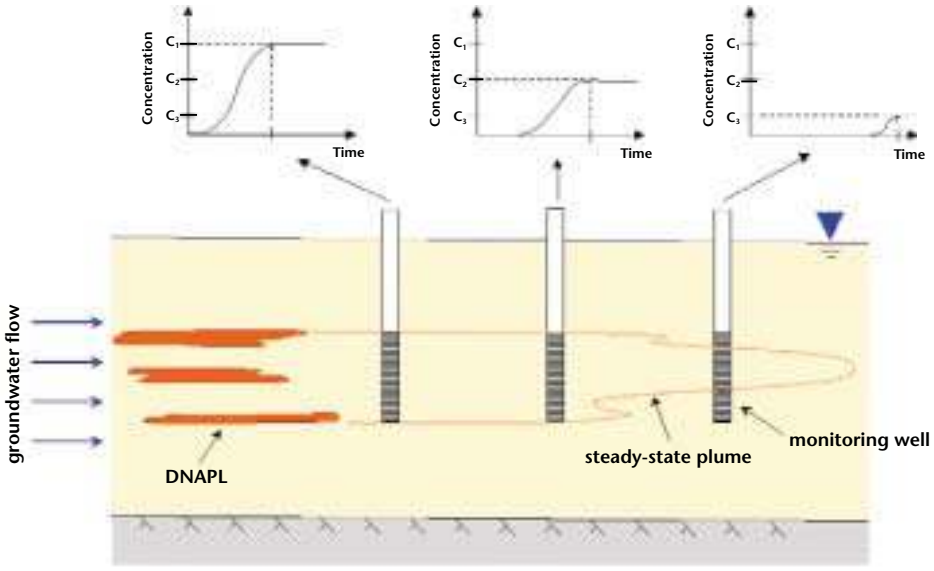


Figure 13 | Development of a steady-state plume

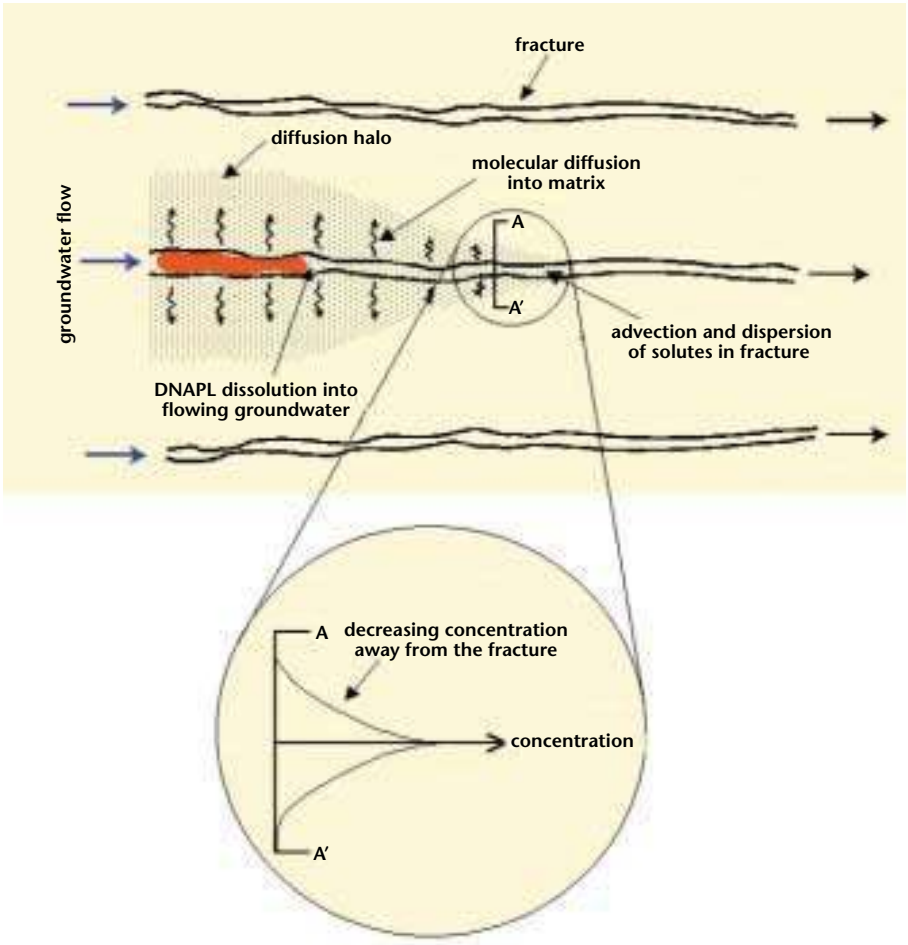


Figure 14 | Matrix diffusion process

This general pattern illustrates that plumes reach steady-state concentrations first near the source and last at the leading edge. If the boundaries of the plume were defined by concentration C_3 (for example, a regulatory limit equal to C_3), then the entire plume will have reached steady-state by time t_3. The precise value of t_3 is site-specific and is influenced by a number of factors including hydraulic conductivity, hydraulic gradient, source zone concentration, sorption and degradation. In general, degradation will lead to shorter steady-state plumes than those arrived at by dispersion alone. Whether a plume has reached steady-state is typically determined through several years of groundwater quality monitoring and/or the use of numerical simulation.

With respect to physical processes influencing plume behaviour, there is one fundamental difference between porous and fractured media. Plumes in fractured clay and rock are subject to a process known as matrix diffusion. Matrix diffusion refers to the process whereby solutes dissolved in groundwater diffuse into and out of the rock matrix. If concentrations are higher in the open fracture, the diffusion process will result in dissolved contaminants moving into the rock matrix (forward diffusion). This is illustrated schematically in **Figure 14**. If concentrations are higher in the rock matrix, dissolved contaminants will move out of the rock matrix and into water in the open fractures (back diffusion). Matrix diffusion will occur in all rock types exhibiting a finite matrix porosity. The diffusion process will therefore occur in virtually all chalk and sandstone rock types in the UK, in clay deposits and in some weathered crystalline rock environments.

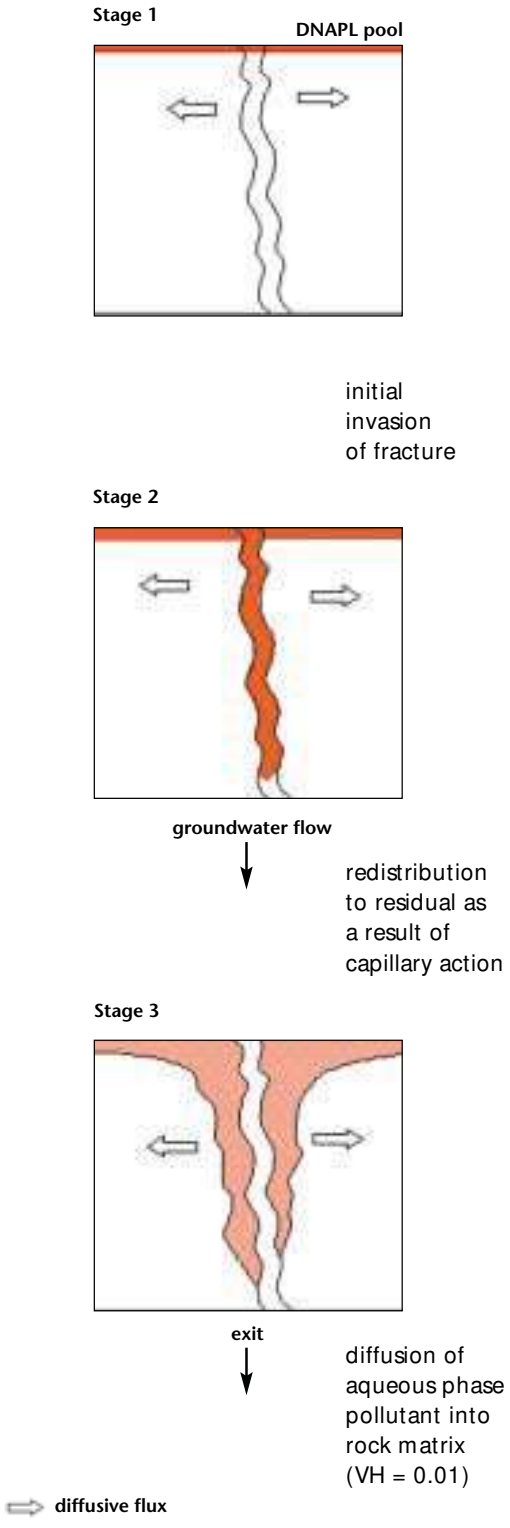


Figure 15 DNAPL release and subsequent depletion by dissolution into a single fracture

One manifestation of the matrix diffusion process is that solute plumes in fractured rock and clay will migrate slower than the rate of groundwater flow. The rate of plume advance in fractured chalk, clay and sandstone can therefore be significantly attenuated relative to the rate of groundwater migration, with attenuation rates as high as 100 or more. The attenuation is greater for smaller aperture fractures, higher matrix porosity and slower moving groundwater. This explains why solute plumes in fractured (dual porosity) environments are often smaller in spatial extent than predicted by groundwater velocity calculations alone.

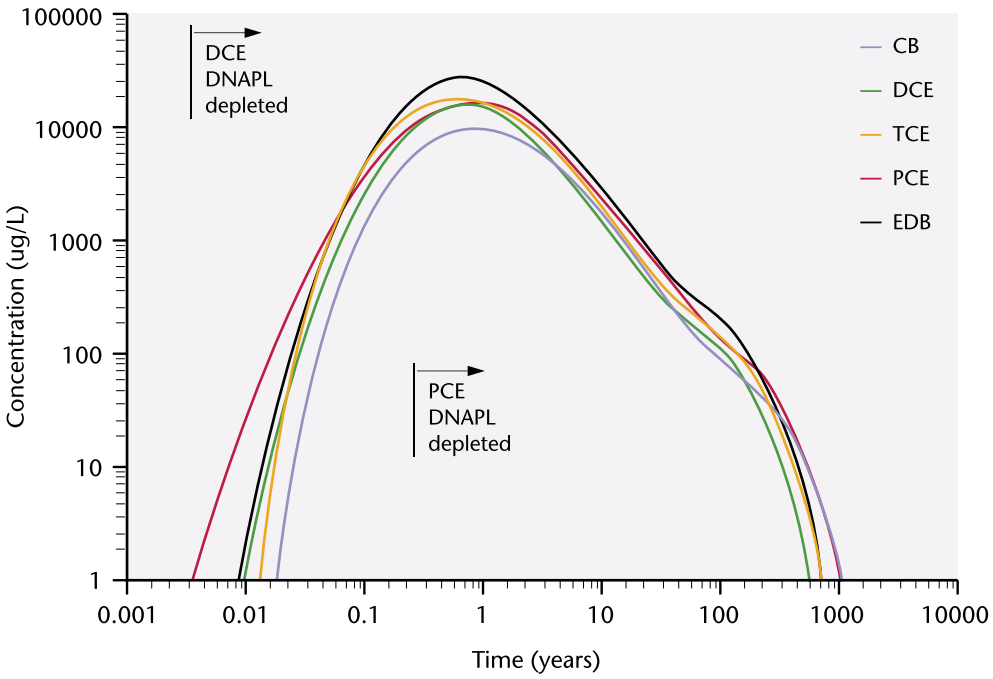
A second manifestation of the matrix diffusion process is that the timescale of remediation in fractured rocks is often controlled by the back diffusion process and not by the presence of DNAPL in fractures. Even for relatively short initial exposure times, the back diffusion process can continue for many decades. Consider the release of a small volume of DNAPL into a single fracture in clay as illustrated in **Figure 15**.

As a result of diffusion into the matrix and dissolution into groundwater flowing through the fracture, the DNAPL is eventually completely depleted. Groundwater concentrations at the exit to the fracture will exhibit measurable concentrations for long periods as a result of back diffusion from the matrix.

Figure 16 (adapted from Reynolds and Kueper, 2002) presents the concentrations of five chlorinated solvents at the exit of the fracture illustrated in **Figure 15** as a function of time.

The fracture is assigned an aperture of 30 µm, a dip of 60˚ below horizontal and a length of 3m. It was assumed in each case that the DNAPL of interest was introduced to the fracture at t = 0(Stage 1 in **Figure 15**), allowed to redistribute to residual DNAPL (Stage 2), and then allowed to dissolve completely into flowing groundwater and diffuse into the clay matrix (Stage 3). The fracture is subject to clean water injection at the top of the system after Stage 2, producing flow in a downwards direction.

Figure 16 shows that measurable exit concentrations



Key: CB = chlorobenzene; DCE = dichloroethene;TCE = trichloroethene; PCE = tetrachloroethene, EDB = 1,2-dibromomethane

Figure 16 | Concentration versus time at exit of fracture (from Reynolds and Kueper, 2002)

persist for many hundreds of years as a result of the back-diffusion process. Although the residual DNAPL dissolved itself out of existence in less than 21 weeks in all cases, the exit concentrations persist for long periods because the back-diffusion process is slower than the initial forward-diffusion process. This stems from the fact that solutes are continuing to migrate further into the clay matrix while at the same time diffusing back into the open fracture after the DNAPL has completely dissolved itself away. In addition, the concentration gradient driving back-diffusion is typically less than the initial concentration gradient driving forward-diffusion into the matrix while residual DNAPL is present in the fracture.

The implication of matrix diffusion in fractured clay and rock is that solute plumes, as well as DNAPL source zones, are difficult to remediate. In fractured environments exhibiting matrix diffusion, conventional technologies such as pump-and-treat should be viewed as either a source zone containment technology, or a plume interception technology, not as a technology capable of restoring groundwater to near-pristine quality within short periods of time. The effectiveness of many remedial techniques is diffusion limited and this process needs to be considered during development of a remedial strategy, and selection of a remedial technique.

7

Determination of DNAPL presence and delineation of the DNAPL source zone

A primary goal of many site investigations is to establish whether DNAPL is present in the subsurface and, if so, to determine the spatial extent of the DNAPL source zone.

DNAPL presence is often established on the basis of converging lines of evidence rather than direct visual observation. The tortuous and sparse nature of DNAPL migration pathways, together with the fact that boreholes and other invasive procedures typically only physically access a minute fraction of the subsurface, result in a low probability of actually encountering DNAPL in many site investigations. Thus, DNAPL is often not observed directly at many DNAPL sites. The overall extent of the source zone should typically be delineated at a site, and not the specific locations of individual DNAPL pools and zones of residual DNAPL within the overall source zone.

The following investigative techniques are typically employed in establishing DNAPL presence at a site.

7.1 Site use/site history

Site investigations should always begin with a desk study; this may start with employee interviews and record searches to establish what operations have taken place at the site (BSI, 2001). **Table 6** lists a variety of industries and industrial processes that are often, but not necessarily, associated with the presence of DNAPLs in the subsurface. Further guidance can be found in the Industry Profile series (DoE, 1995) produced by former Department of the Environment (now the Department for Environment, Food and Rural Affairs).

Table 6 Table 6 Industries and industrial processes sometimes associated with DNAPL presence in the subsurface (modified from US EPA, 1992)

Industries	Industrial processes
Timber treatment	Metal cleaning and degreasing
Coal gasification (Town gas production)	Metal machining and plating
Electronics manufacturing	Tool-and-die operations
Solvent or paint production	Paint removing
Pesticide/herbicide manufacturing	Solvent storage above or below ground
Aeroplane maintenance and engine manufacturing	Solvent transmission through piping
Military bases and rocket fuel production	Solvent loading and unloading
Dry cleaning	Disposal of mixed wastes in landfills
Instrument manufacturing	Storage of liquid wastes in lagoons and ponds
Transformer oil production	
Vehicle manufacturing	
Transformer reprocessing	
Steel industry coking	
Pipeline compressor stations	

7.2 Aerial photographs, maps and plans

If available, aerial photographs, maps and plans can be examined to determine if drum storage areas, railway unloading areas, above ground storage tanks, evaporation ponds, etc. were present at the site. Such features may represent potential DNAPL entry points into the subsurface.

7.3 Screening of soil borings

Soil samples can be taken from unconsolidated deposits both above and below the water table using a variety of techniques such as hollow stem auguring, push sampling and trial pits. During drilling operations, soil samples can be taken and subjected to visual examination. If DNAPL is present at high saturations (that is, pooled DNAPL) it will be probably be readily noticeable. If the DNAPL is present at low saturations (that is, residual saturation) or if the DNAPL has the same colour as the soil matrix, it may not be visually apparent and a dye shake test may be required.
A dye shake test involves mixing a small quantity of a hydrophobic dye such as SUDAN IV with the soil sample in a sealed glass jar. In the case of SUDAN IV, the dye is red in colour and will partition only into a NAPL phase; it will not partition into water. If a NAPL is present in the soil sample, it will manifest itself as red globules interspersed within the soil matrix.
Other field screening methods for soil borings include headspace analysis using a portable vapour analyser with photoionisation detection (PID) or flame ionisation detection (FID), and the use of fluorescence analysis. Fluorescence analysis involves taking the obtained soil sample and subjecting it to a fluorescent light in a dark space. Many hydrocarbons such as aromatic and polyaromatic hydrocarbons having one or more benzene rings (for example, coal tar, creosote and PCBs) will fluoresce, along with DNAPL mixtures containing petroleum products and certain unsaturated aliphatic hydrocarbons such TCE and PCE.

7.4 Screening of rock cores

Bedrock drilling techniques are typically very aggressive due to the high temperatures and high water velocities that are usually generated in the immediate vicinity of the boring. The DNAPL is generally pushed out of rock fractures before the core is retrieved at ground surface. It is therefore unreasonable to expect DNAPL to be present in a fracture in rock core, even when drilling directly through fractures that originally contained residual DNAPL or pools. Possible exceptions may be creosote or coal tar, which tend to be more viscous than other DNAPLs. In some cases, however, the DNAPL may have stained the rock fracture walls, which may be discernible upon inspection of the core. However, not all DNAPLs will stain fracture walls. Consequently, the absence of staining should not be relied on as unequivocal evidence that the fracture has not been exposed to DNAPL. Additional screening techniques when drilling in bedrock include inspecting the drill return water for visual or olfactory evidence of hydrocarbons (for example, iridescent sheens or odours) and headspace analysis of rock core that may contain high concentrations of contaminants diffused into the matrix. Exposure to hazardous substances should, however, be controlled and sniffing cores is not appropriate unless it is clear that it is safe to do so. Prior use of calibrated PID/FID equipment may be appropriate where there is any doubt.

7.5 Laboratory analysis of soil samples

Soil characterisation programmes typically involve sending discrete soil samples to the laboratory for quantitative analysis of contaminant composition. The presence of NAPL in a soil sample can be evaluated using:

Equation 2

$$C_i^T = \frac{C_i}{P_b}\left(K_d P_b + \theta_w + H'\theta_a\right)$$

where:

- C_i^T is the concentration of an organic substance at or above that which may be present in a non-aqueous phase (mg/kg);
- C_i is the effective solubility of the substance in groundwater (mg/l);
- P_b is the dry soil bulk density (kg/l);
- K_d is the soil-water partition coefficient (l/kg);
- θ_w is the water-filled porosity (dimensionless);
- H' is the unitless Henry's law constant (dimensionless);
- θ_a is the air-filled porosity.

The soil-water partition coefficient is often approximated by:

Equation 3

$$K_d = K_{oc} f_{oc}$$

where:

K_{oc} is the organic carbon-water partition coefficient (l/kg);

f_{oc} is the fraction organic carbon present in the soil (dimensionless).

For structurally similar compounds in a multi-component NAPL, the effective solubility, *Ci*, can be estimated using Equation 1 (see Section 4).

Equation 2 represents the maximum amount of contaminant that can be present in a soil sample in the sorbed, aqueous and vapour phases without a NAPL phase being present. If reported soil concentrations exceed C_i^T, it can be concluded that a NAPL phase was present in the sample. **Table 7** presents an example calculation of the above procedure for a single component DNAPL composed of TCE located below the water table. This calculation procedure assumes that the composition of the DNAPL is known, a priori, such that the required mole fractions can be determined. If the DNAPL is known to be composed of primarily one component, the mole fraction of that component can be assumed to be one. At sites where a multi-component DNAPL is suspected and a DNAPL sample has not been obtained for component composition analysis, the required mole fractions will not be known. In such cases, this calculation procedure can still be employed, but with a slight modification.

Table 7 Example calculation of soil DNAPL threshold concentration: single component DNAPL below the water table

TCE solubility in water = 1,100 mg/l

Fraction organic carbon of soil = 0.003

Porosity of soil = 0.27

K_{oc} of TCE = 126 l/kg

Dry bulk density of soil = 1.9 kg/l

Air filled porosity = 0

$$C_{TCE}^T = \frac{1100}{1.9}\left(126(0.0031)1.9 + 0.27\right) = 572 \text{ mg/kg}$$

For a multi-component DNAPL of unknown composition, the sum of the mole fractions must equal one. DNAPL will therefore be present in a soil sample if the following condition is met:

Equation 4

$$\sum_{i=1}^{n} \frac{C_{obs}^T}{C_S^T} \geq 1$$

where:

C_{obs}^T is the reported concentration of component *i*;

C_S^T is the single component soil concentration of component *i*;

n is the total number of components observed in the soil sample.

Appendix C presents an example calculation using a soil sample containing five different compounds.

7.6 Bailers and interface probes

In addition to water level and groundwater quality monitoring, monitoring wells and piezometers can be inspected for the presence of DNAPL using bottom-loading bailers and weighted oil-water interface probes.

7.7 Contaminant concentrations in groundwater

As discussed in Section 4, experience has shown that DNAPL may be present up – gradient of a monitoring well displaying sampled groundwater concentrations in excess of 1 per cent of the effective solubility of the component of interest. Calculating the 1 per cent effective solubility requires a priori knowledge of the DNAPL composition such that mole fractions can be established. If the DNAPL is thought to be composed of primarily one component, the mole fraction of that component can be approximated to be one. If the DNAPL is thought to be composed of several components, however, a modified approach will be required in cases where a DNAPL composition analysis is not available.

For a multi-component DNAPL dissolving into groundwater, the equilibrium aqueous phase concentration can be represented using Raoult's law as presented in Equation 1 (see Section 4).

Because groundwater concentrations are typically obtained from monitoring well samples, a certain degree of dilution will occur due to borehole dilution, hydrodynamic dispersion, non-optimal well placement and degradation. In this analysis, the degree of dilution due to these three processes will be represented by the parameter *a*, such that:

Equation 5

$$a = \frac{C_i^{obs}}{C_i}$$

where:

C_i^{obs} is the concentration observed in the monitoring well;

C_i is the effective solubility given by Equation 1.

For a multi-component DNAPL, the sum of the mole fractions must equal one:

Equation 6

$$\sum \frac{C_i}{S_i} = 1$$

Combining Equations 5 and 6 yields:

Equation 7

$$\sum \frac{C_i^{obs}}{S_i} = a$$

If there were no effects from borehole dilution, dispersion, degradation or monitoring well placement, the parameter *a* would equal one in the vicinity of a multi-component NAPL. However, because these processes all occur to some degree, *a* will take on a value less than one. If the 1 per cent 'rule-of-thumb' is adopted, it follows that DNAPL may be present upstream of a monitoring well if $a > 0.01$. This assumes that the degree of borehole dilution, dispersion and degradation is identical for each component of interest. This is likely to be the case for borehole dilution and dispersion, but may not be the case for degradation. For monitoring wells in close proximity to DNAPL, however, the amount of degradation may be minimal such that the error introduced by varying amounts of degradation will be negligible.

Equation 7 can be applied on a sample-by-sample basis without having to assume that the NAPL composition is spatially uniform. In addition, the parameter *a* can be any value less than one. If it is believed that 10 per cent of the effective solubility indicates NAPL presence, for example, *a* can be set to 0.1. **Table 8** presents an example calculation where five components have been detected in a monitoring well. Although each component has been detected at a concentration less than 1 per cent of the single component solubility, the cumulative mole fractions add up to 3.4 per cent, providing evidence of possible DNAPL presence upstream of the monitoring location.

7.8 Presence of contamination in hydraulically anomalous locations

Figure 2 presents a schematic illustration of DNAPL presence in the subsurface. Given that groundwater is flowing from left to right in the figure, it is not possible for DNAPL sources in the unsaturated zone alone to give rise to aqueous phase contamination deep in the overburden or in the fractured bedrock. If a flow line cannot be drawn between known shallow sources and deeper, up-gradient or side-gradient occurrences of aqueous phase contamination, a DNAPL source may be present up-gradient of those

Table 8 | Example calculation of cumulative mole fraction in a groundwater sample

Compound	Concentration in monitoring well (mg/l)	Single component solubility (mg/l)	C_iS_i
trichloroethene	4.4	1100	0.004
tetrachloroethene	1.8	200	0.009
toluene	3.5	500	0.007
chlorobenzene	4.0	500	0.008
trichloromethane	48.0	8000	0.006
$\sum \frac{C_i^{obs}}{S_i}$			**0.034**

monitoring locations. A classic example of this is the presence of groundwater contamination at depth in a flow field characterised by an upward component to flow. If groundwater is flowing up from depth (for example in a groundwater discharge zone) and aqueous phase contamination is encountered at depth, the source of that contamination will be hydraulically up-gradient (that is, deeper) of the monitoring well in question

7.9 Persistence of contamination

If contamination persists at a particular monitoring location, it follows that a stable source of contamination such as DNAPL may be present hydraulically up-gradient of that location. If contaminant releases took place 20 years ago, for example, and the groundwater velocity at the site was 50 m/year, one would expect a non-sorbing aqueous phase contaminant to have travelled approximately 1,000 m in the 20-year period. If contamination is still connected to the source area with generally decreasing concentrations in the down-gradient direction, a stable source of contamination is likely to be feeding the plume.

7.10 Persistence of alcohols in groundwater

If readily degradable co-solvents such as alcohols are detected in monitoring wells, it is likely that they are derived from a stable source such as residual or pooled DNAPL. Alcohols are known to partition into both groundwater and NAPL phases. It is also known that alcohols tend to biodegrade readily in many groundwater environments. If alcohols are detected regularly in a particular monitoring well, it is possible that a DNAPL source is supplying the alcohols to groundwater.

Considerable uncertainty will exist with respect to delineating the DNAPL source zone. Establishing whether DNAPL is present at a site is typically easier than delineating the exact spatial extent of the DNAPL source zone. It is advisable to adopt a two-tiered approach.

Figure 17 illustrates both a probable and a potential DNAPL zone. The probable DNAPL zone encompasses that volume of the subsurface where many converging lines of evidence suggest DNAPL presence. These may include the locations of former known DNAPL storage and release areas such as evaporation ponds and drum disposal areas, locations where DNAPL has been visually observed in soil samples, locations where soil concentrations are above the calculated DNAPL threshold, and locations where groundwater concentrations are very high (for example, over 10 per cent effective solubility). The potential DNAPL source zone provides a factor of safety, and may represent the volume of the subsurface where fewer converging lines of evidence suggest DNAPL presence.

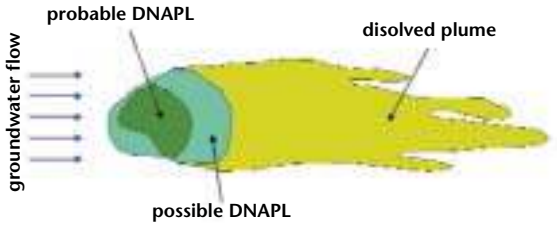


Figure 17 Probable and potential DNAPL zones

Both the estimated extent of the probable and potential DNAPL source zones should be updated, along with other aspects of the site conceptual model, whenever new data become available (Environment Agency, 2001a). It is unreasonable to expect site investigation techniques to be able to define the lateral and vertical extent of the DNAPL source zone exactly; regardless of the level of data collection, uncertainty will always exist.

With respect to drilling strategies, it is recognised that drilling directly through a DNAPL source zone carries with it a significant risk of mobilising DNAPL deeper into the subsurface. Many practitioners adopt an outside-in approach in which monitoring wells are first placed outside the suspected DNAPL source zone. Subsequent borings are added closer and within the source area on an as-needed basis until the source zone location has been defined in sufficient detail to satisfy the investigation objectives. In some drilling programmes, a contingency plan is provided in case strong evidence of the presence of DNAPL is gathered during drilling operations. Such a plan may involve terminating boreholes or moving to an alternative drilling location whenever mobile DNAPL is encountered. It is also customary to install sumps at the base of monitoring wells and piezometers suspected of being in close proximity to DNAPL sources. The sumps facilitate the collection of DNAPL and avoid DNAPL exit from the bottom of the well following entry into the well at a higher elevation.

UK Specific Conceptual Models

8.1 Chlorinated solvent release into Cretaceous Chalk

Figure 18 illustrates a release of chlorinated solvent DNAPL at the ground surface into shallow drift deposits overlying fractured Cretaceous chalk. In the drift, residual and pooled DNAPL have migrated laterally in all directions in response to the bedding structure of the unconsolidated deposits. Due to the volatile nature of the solvent DNAPL, a well-defined vapour plume has developed. Depending on the bedding structures, soil sampling to determine DNAPL presence may be a 'hit and miss' proposition because of the tortuous and sparse nature of DNAPL migration pathways. Soil vapour sampling may be a more efficient way of determining the lateral extent of the source zone in the drift deposit, where the DNAPL gives rise to vapours.

The volume of the DNAPL release was sufficient to reach the top of bedrock, which is characterised by weathered chalk. DNAPL has entered the fractured chalk and, because of the low fracture porosity, has migrated to considerable depth. The depth of DNAPL migration cannot be determined easily because of the large number of boreholes required, the high cost and the risk of dragging contamination deeper into bedrock. DNAPL has come to rest primarily as pooled DNAPL in the horizontal fractures and as residual DNAPL in the vertical and steeply dipping fractures.

DNAPL is restricted to fractures below the water table and has not entered the chalk matrix as a separate liquid phase because of the high entry pressure associated with the narrow pore throat size in a chalk matrix. Above the water table, however, some areas of the chalk matrix have very low water saturations and limited DNAPL migration into the matrix has occurred. DNAPL has migrated preferentially in the larger aperture fractures and has spread laterally in all directions, including hydraulically up-gradient of the release location. Because of the high density and low viscosity of the chlorinated solvent DNAPL, migration through the subsurface was rapid and ceased within a relatively short time period following the entry of DNAPL into bedrock. Groundwater flow through the fractures containing residual and pooled DNAPL has brought about DNAPL dissolution and the evolution of a dissolved phase plume.

The plume is migrating through the set of interconnected fractures subject to advection, dispersion, a limited amount of biodegradation, and matrix diffusion. Because of matrix diffusion, the plume has not migrated as far as would be predicted by simple groundwater velocity calculations. At this site, the plume is migrating 50 – 500 times slower than the groundwater, with greatest attenuation in the smaller aperture fractures. Diffusion of aqueous phase contaminants into the Chalk matrix is also occurring immediately adjacent to the residual and pooled DNAPL, where concentration gradients are greatest. With time, a greater and greater portion of the mass is transferred from the open fractures to the matrix. In the smaller aperture fractures, the DNAPL has completely diffused into the matrix.

With respect to site characterisation, efforts below the water table are focused on defining the spatial extent of the aqueous phase plume and establishing whether it has reached a steady-state configuration. Limited drilling is taking place within the DNAPL source zone. The extent and depth of the source zone in bedrock are being inferred on the basis of the spatial distribution of groundwater concentrations downstream of the source zone. In the case of a single component DNAPL, groundwater sampling is focused on the contaminant of interest and its daughter products. In the case of a multi-component DNAPL, groundwater sampling includes the most mobile component(s) of the DNAPL since they will define the leading edge of the plume, but may also include less mobile compounds that present a potential risk to human health and the environment. The most mobile component of the DNAPL is taken to be a component that is present at detectable concentrations, sorbs little, and is not subject to appreciable amounts of degradation.

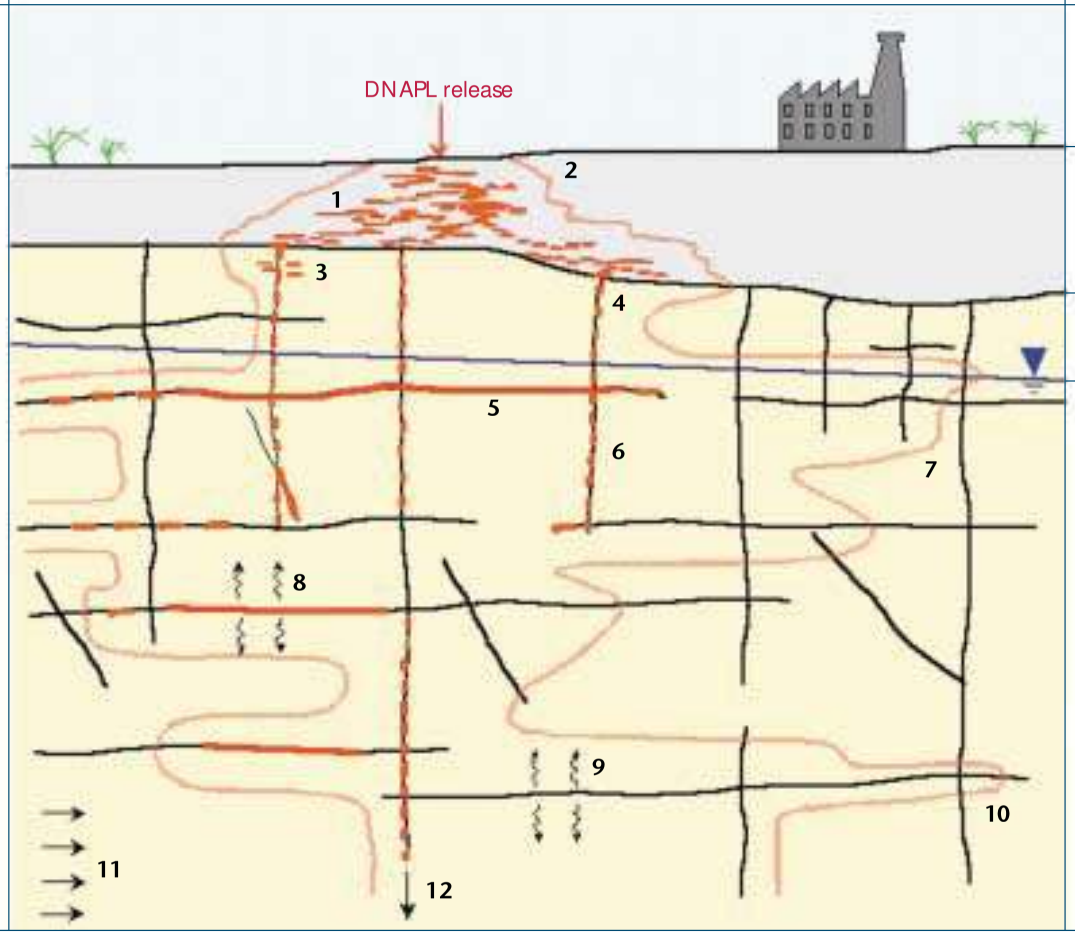
Features	Release of chlorinated solvent DNAPL into Cretaceous Chalk	Domain
1 Residual and pooled DNAPL in drift **2** Vapour **3** DNAPL migration into unsaturated chalk **4** Matrix diffusion and advective vapour **5** Pooled DNAPL in fractures **6** Residual DNAPL in fractures **7** Extent of groundwater plume **8** Matrix diffusion next to DNAPL **9** Aqueous phase diffusion into matrix **10** Advection and dispersion of contaminants in fractures **11** Groundwater flow direction **12** DNAPL migration to depth		**Surface** **Drift** (unsaturated) **Bedrock** (unsaturated) **Bedrock** (saturated)

Figure 18 | Release of chlorinated solvent DNAPL into Cretaceous Chalk

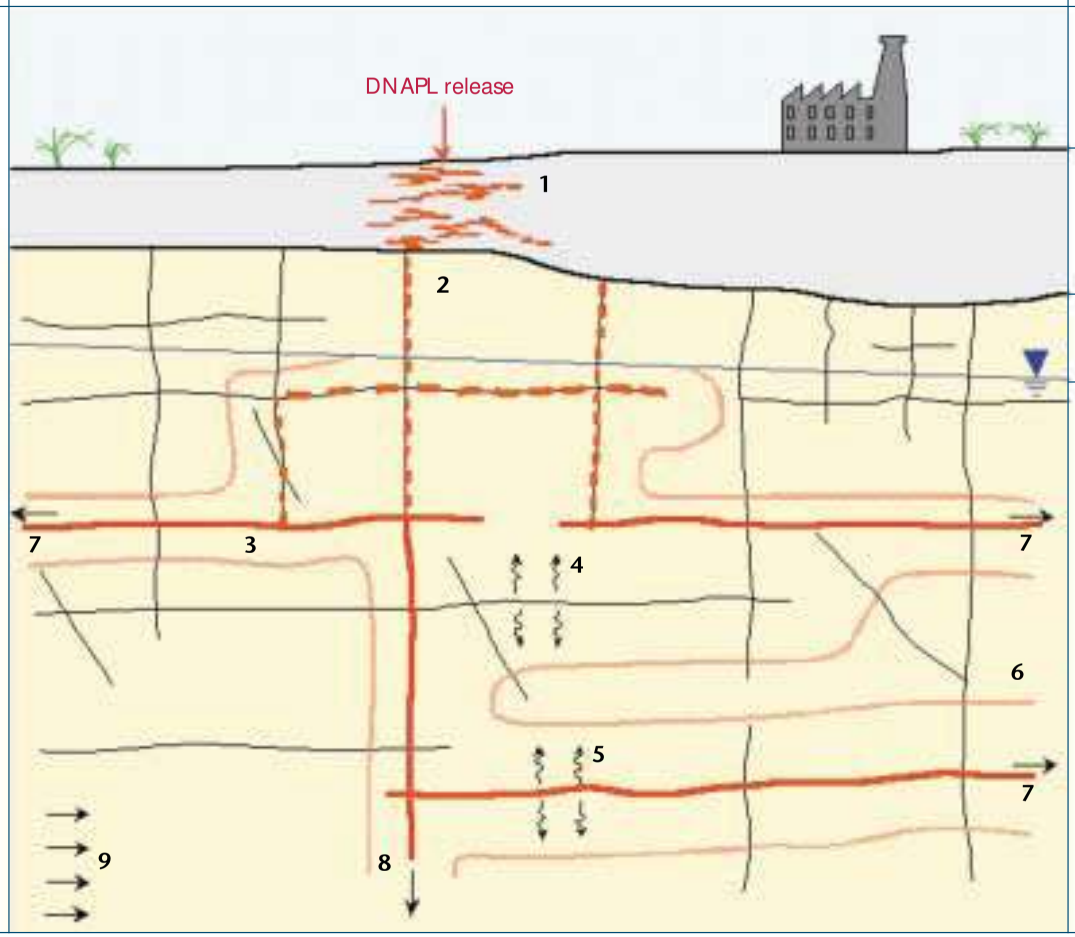
Features	Release of coal tar DNAPL into Cretaceous Chalk	Domain
1 Residual and pooled DNAPL in drift 2 Residual DNAPL in fractures 3 Pooled DNAPL in fractures 4 Aqueous phase diffusion into matrix 5 Diffusion into matrix next to DNAPL 6 Plume extent 7 On-going DNAPL migration (lateral) 8 Ongoing DNAPL migration (vertical) 9 Groundwater flow direction		Surface Drift (unsaturated) Bedrock (unsaturated) Bedrock (saturated)

Figure 19 | Release of coal tar DNAPL into Cretaceous Chalk

8.2 Coal tar release into Cretaceous Chalk

Figure 19 illustrates a release of coal tar DNAPL at the ground surface into shallow drift deposits that overlie fractured Cretaceous Chalk. The coal tar release took place during the early part of the 20th century at a coal gas manufacturing facility. In the overburden, residual and pooled DNAPL have migrated laterally in all directions in response to the bedding structure of the unconsolidated deposits. A well-defined vapour plume is not present because the highly volatile components of the coal tar were preferentially depleted at an early time, leaving only low volatility components of the DNAPL in the drift.

Although soil sampling can be a 'hit and miss' exercise depending on bedding structures, it is still the most practical way to define the lateral extent of the source zone in the unconsolidated deposits, where the DNAPL does not readily give rise to vapours.

The volume of the DNAPL release was sufficient to reach the top of the bedrock, which is characterised by weathered chalk. DNAPL has entered the fractured chalk and, because of the low fracture porosity, has migrated to a considerable depth. DNAPL migration is still occurring today due to the relatively low density and high viscosity of the DNAPL, and because large volumes of coal tar were released. The depth of DNAPL migration cannot be determined easily because of the large number of boreholes required, but limited drilling will take place in the source zone to determine if the DNAPL is still in a mobile form. Monitoring wells will be completed with sumps below the well screen to facilitate the collection of mobile DNAPL. In many places, DNAPL has already come to rest primarily as pooled DNAPL in the horizontal fractures and as residual DNAPL in the vertical and steeply dipping fractures. DNAPL is restricted to fractures below the water table and has not entered the chalk matrix as a separate liquid phase because of the high entry pressure. Above the water table, however, some areas of the chalk matrix are very dry and limited DNAPL migration into the matrix has occurred. DNAPL has migrated primarily in the larger aperture fractures and has spread laterally in all directions, including hydraulically up-gradient of the release location. The amount of lateral spreading is greater than that for the chlorinated solvent DNAPL release depicted in **Figure 18** because of the lower density of the DNAPL.

Groundwater flow through the fractures containing residual and pooled DNAPL has brought about DNAPL dissolution and the evolution of a dissolved phase plume. The plume is migrating through the set of interconnected fractures subject to advection, dispersion, biodegradation and matrix diffusion. Because of the matrix diffusion process, the plume has not migrated as far as would be predicted by groundwater velocity calculations. At this site, the plume is migrating 50 – 500 times slower than the groundwater with higher amounts of attenuation in the smaller aperture fractures. Diffusion of aqueous phase contaminants into the chalk matrix is also occurring immediately adjacent to the residual and pooled DNAPL. With time, a greater and greater portion of the mass is transferred from the open fractures to the matrix.

With respect to site characterisation, efforts below the water table are focused on defining the spatial extent of the aqueous phase plume and establishing whether it has reached a steady-state configuration. Although some drilling is taking place within the DNAPL source zone, the extent and depth of the source zone in the chalk is being inferred largely on the basis of the spatial distribution of groundwater concentrations downstream of the source zone. Because the coal tar release occurred several decades ago, the more mobile, low molecular weight components of the DNAPL no longer represent the major constituents of the plume. A few indicator compounds are selected to define the extent of the plume; because of their low mobility, the dissolved plume is not expected to have advanced far ahead of the DNAPL source zone.

8.3 Chlorinated solvent release into Triassic Sandstone

Figure 20 depicts a release of chlorinated solvent DNAPL at the ground surface into shallow drift deposits overlying fractured sandstone. In the overburden, residual and pooled DNAPL have migrated laterally in all directions in response to the bedding structure of the unconsolidated deposits. Because of the volatile nature of the solvent DNAPL, a well-defined vapour plume has developed. Depending on the bedding structures, soil sampling to determine DNAPL presence may be a 'hit and miss' proposition due to the tortuous and sparse nature of DNAPL migration pathways. Soil vapour sampling may be a more efficient way to determine the lateral extent of the chlorinated solvent source zone in the drift deposit.

The volume of the DNAPL release was sufficient to reach the top of bedrock. DNAPL has entered the fractured sandstone and, due to the low fracture porosity, has migrated to a considerable depth. The depth of DNAPL migration cannot be determined easily because of the large number of boreholes

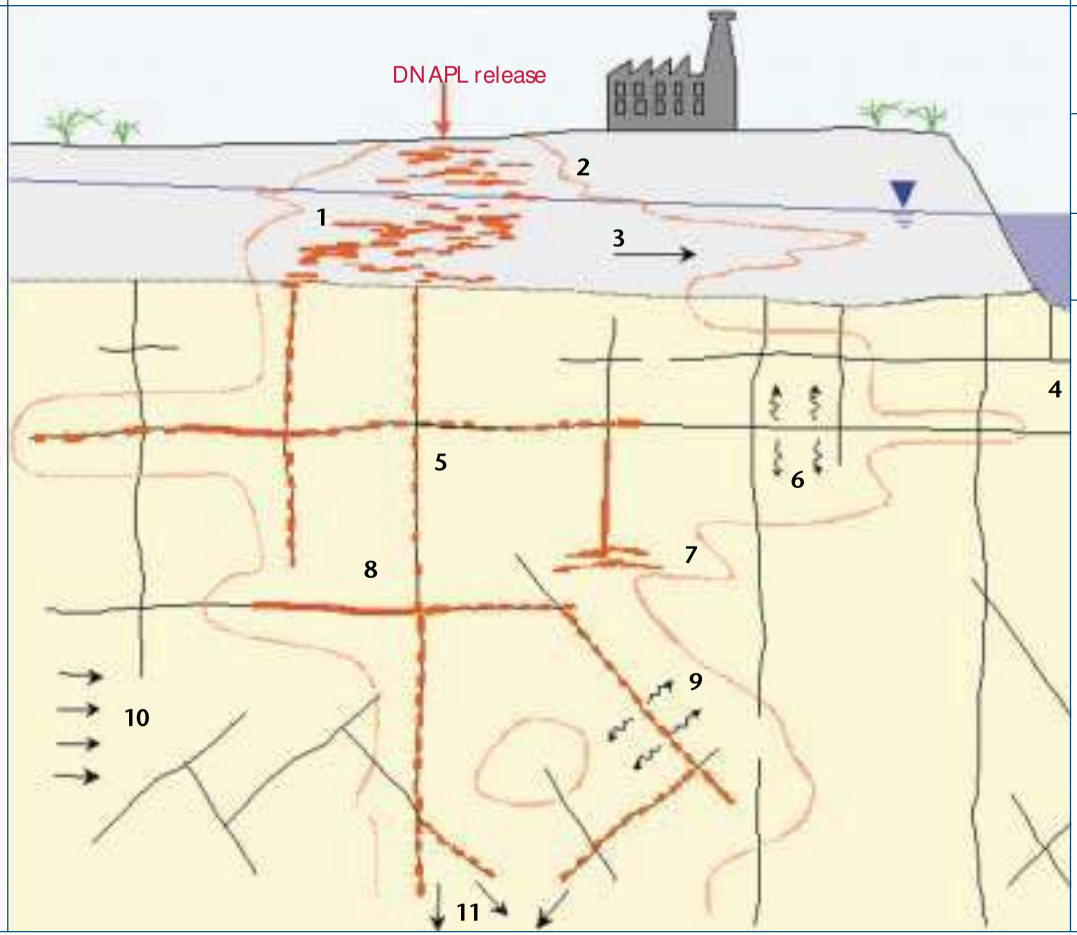
Features	Release of chlorinated solvent DNAPL into Triassic Sandstone	Domain
1 Residual and pooled DNAPL in drift 2 Vapour 3 Aqueous phase plume migration 4 Aqueous phase plume migration in fracture 5 Residual DNAPL in fractures 6 Aqueous phase matrix diffusion 7 DNAPL penetration into coarse grained matrix 8 Pooled DNAPL in fractures 9 Matrix diffusion adjacent to DNAPL 10 Groundwater flow direction 11 DNAPL migration to depth		**Surface** **Drift** (unsaturated) **Drift** (saturated) **Bedrock** (saturated)

Figure 20 | Release of chlorinated solvent DNAPL into Triassic Sandstone

needed, the high cost and the risk of dragging contamination deeper into bedrock and creating new conduits. DNAPL has come to rest primarily as pooled DNAPL in the horizontal fractures and primarily as residual DNAPL in the vertical and steeply dipping fractures. DNAPL is not necessarily restricted to fractures below the water table and has entered the sandstone matrix as a separate liquid phase where the matrix is composed of weakly cemented, coarse-grained sediments. Above the water table, DNAPL has entered those regions of the rock matrix that exhibit continuous air pathways and those composed of coarse-grained sediments.

DNAPL has migrated primarily in the larger aperture fractures and has spread laterally in all directions, including hydraulically up-gradient of the release location. The angled nature of the fractures in some regions has led to preferential migration in the down-dip direction. Because of the high density and low viscosity of the chlorinated solvent DNAPL, migration ceased within a relatively short time following entry of DNAPL into the bedrock.

Groundwater flow through the fractures containing residual and pooled DNAPL has brought about DNAPL dissolution and the evolution of a dissolved phase plume. The plume is migrating through the set of interconnected fractures subject to advection, dispersion, a limited amount of biodegradation, and matrix diffusion. Because of the matrix diffusion process, the plume has not migrated as far as would be predicted by groundwater velocity calculations. At this site, the plume is migrating 50 – 500 times slower than the groundwater with higher amounts of attenuation in the smaller aperture fractures. Diffusion of aqueous phase contaminants into the sandstone matrix is also occurring immediately adjacent to the residual and pooled DNAPL. With time, a greater and greater portion of the mass is transferred from the open fractures to the matrix.

With respect to site characterisation, efforts below the water table are focused on defining the spatial extent of the aqueous phase plume and establishing whether it has reached a steady-state configuration. Limited drilling is taking place within the DNAPL source zone. The extent and depth of the source zone in the sandstone is being inferred on the basis of the spatial distribution of groundwater concentrations downstream of the source zone. In the case of a single component DNAPL, groundwater sampling is focused on the contaminant of interest and its daughter products. In the case of a multi-component DNAPL, groundwater sampling is focused on the most mobile component(s) of the DNAPL since this will define the leading edge of the plume. The most mobile component of the DNAPL is taken to be a component that is present at detectable concentrations, sorbs little and is not subject to appreciable amounts of degradation.

8.4 Coal tar release into fractured Triassic Sandstone

Figure 21 illustrates a release of coal tar DNAPL at ground surface into shallow drift deposits overlying fractured sandstone.

The coal tar release took place in the early part of the 20th century at a coal gas manufacturing facility. In overburden, residual and pooled DNAPL have migrated laterally in all directions in response to the bedding structure of the unconsolidated deposits. A well-defined vapour plume is not present because the highly volatile components of the coal tar were preferentially depleted at an early time, leaving only the low volatility components of the DNAPL remaining in overburden. Although soil sampling can be a 'hit and miss' exercise depending on bedding structures, it is still the most practical way to define the lateral extent of the source zone in the unconsolidated deposits, where the DNAPL does not give rise to vapours.

DNAPL has entered the fractured sandstone and, because of the low fracture porosity, has migrated to a considerable depth. DNAPL migration is still occurring today due to the low density and high viscosity of the DNAPL, and because large volumes of coal tar were released. The depth of DNAPL migration cannot be determined easily because of the large number of boreholes needed, but limited drilling will take place in the source zone to determine if the DNAPL is still in a mobile form. Monitoring wells will be completed with sumps below the well screen to facilitate the collection of mobile DNAPL. In many places, DNAPL has already come to rest primarily as pooled DNAPL in the horizontal fractures and primarily as residual DNAPL in the vertical and steeply dipping fractures. DNAPL is present primarily in open fractures below the water table, but has also entered the sandstone matrix where it is composed of coarse-grained sediments that exhibit a relatively low entry pressure. Above the water table, some areas of the sandstone matrix are either also coarse grained or very dry, and DNAPL migration into the matrix has occurred.

Below the water table, DNAPL has migrated primarily in the larger aperture fractures and has spread laterally in all directions, including hydraulically up-gradient of

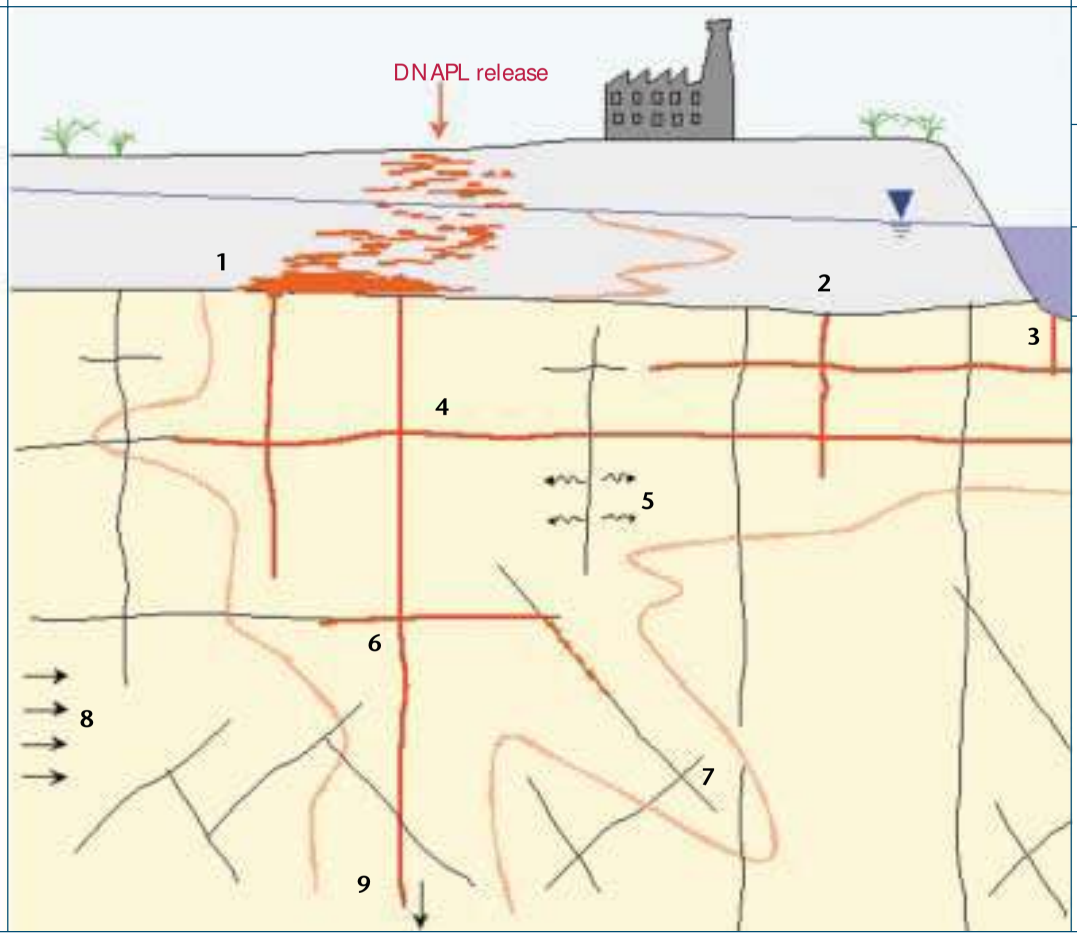
Features	Release of coal tar DNAPL into Triassic Sandstone	Domain
1 DNAPL pool slowly entering fractures 2 Aqueous phase plume formation 3 DNAPL discharge to surface water 4 Pooled DNAPL 5 Matrix diffusion 6 Residual DNAPL 7 Plume in fracture 8 Groundwater flow direction 9 On-going DNAPL migration to depth		**Surface** **Drift** (unsaturated) **Drift** (saturated) **Bedrock** (saturated)

Figure 21 | Release of coal tar DNAPL into Triassic Sandstone

the release location. The amount of lateral spreading is greater than that for the chlorinated solvent DNAPL release depicted in **Figure 20** because of the lower density of the DNAPL. In **Figure 21**, lateral spreading has carried coal tar to a receiving water body. Evidence of DNAPL entry into the water body includes surface sheens and the presence of DNAPL blobs in bottom sediments. The discharge of coal tar to the receiving water body is facilitated by the upward component to groundwater flow in this area. The upward groundwater flow is capable of carrying the coal tar DNAPL upwards against gravity because the DNAPL is only marginally denser than water.

Groundwater flow through the fractures containing residual and pooled DNAPL has brought about DNAPL dissolution and the evolution of a dissolved phase plume. The plume is migrating through the set of interconnected fractures subject to advection, dispersion, biodegradation and matrix diffusion. Because of the matrix diffusion process, the plume has not migrated as far as would be predicted by groundwater velocity calculations. At this site, the plume is migrating 50 – 500 times slower than the groundwater with higher amounts of attenuation in the smaller aperture fractures. Diffusion of aqueous phase contaminants into the sandstone matrix is also occurring immediately adjacent to the residual and pooled DNAPL. With time, a greater and greater portion of the mass is transferred from the open fractures to the matrix.

With respect to site characterisation, efforts below the water table are focused on defining the spatial extent of the aqueous phase plume and establishing whether it has reached a steady-state configuration. Although some drilling is taking place within the DNAPL source zone, the extent and depth of the source zone in the sandstone is being inferred largely on the basis of the spatial distribution of groundwater concentrations downstream of the source zone. Because the coal tar release occurred several decades ago, the more mobile, low molecular weight components of the DNAPL no longer represent the major constituents of the plume. A few indicator compounds are selected to define the extent of the plume and, because of their low mobility, the plume is not expected to have advanced far ahead of the DNAPL source zone.

8.5 DNAPL release into a thin veneer of clay-rich till

Figure 22 illustrates a surface release of DNAPL into clay-rich till overlying Cretaceous Chalk.

The relatively thin veneer of clay till contains vertical fractures, root holes and sand seams that provide preferential pathways for DNAPL migration. Residual and pooled DNAPL is retained in these pathways and DNAPL entry into the underlying fractured bedrock occurs. Their sparse nature means that DNAPL migration pathways may not be encountered directly by site characterisation efforts conducted in the clay till.

The porous nature of the till matrix allows for a degree of migration of vapours in unsaturated regions of the till, dependant on site-specific conditions, and for aqueous phase diffusion of contaminants in water-saturated regions. Soil sampling conducted in the till may reveal low levels of contamination associated with the diffusion halos originating from the fractures and sand seams. The use of angled borings can increase the probability of encountering vertical fractures. Significant amounts of lateral DNAPL migration can occur in all directions if horizontal pathways such as sand seams are laterally extensive and connected. The degree of lateral DNAPL migration is greater for lower density DNAPLs such as creosote and coal tar, and less for high density DNAPLs such as chlorinated solvents. With respect to plume migration, matrix diffusion into the clay matrix will significantly retard the rate of aqueous phase contaminant migration relative to the rate of groundwater flow.

8.6 DNAPL release into a thick sequence of clay-rich till

Figure 23 illustrates a surface release of DNAPL into a thick sequence of clay rich till. The till unit contains both vertical fractures and sand seams which provide pathways for lateral and vertical DNAPL migration. The frequency of fracturing decreases with depth, causing greater amounts of lateral DNAPL spreading at shallow depth. As in **Figure 22**, the directions of lateral DNAPL spreading are dictated primarily by geological structure and not the direction of groundwater flow. In cases where the till unit is exceptionally thick, it is possible that DNAPL could not penetrate the sequence. In practice, however, it should be assumed that DNAPL has traversed clay till sequences unless groundwater sampling beneath the till unit (with appropriate seals around boreholes to prevent migration down the hole) reveals an absence of contamination.

Like **Figure 22**, residual and pooled DNAPL are retained in the fractures and sand seams that transmitted DNAPL. Given their sparse nature, DNAPL migration pathways may not be encountered directly by site characterisation efforts.

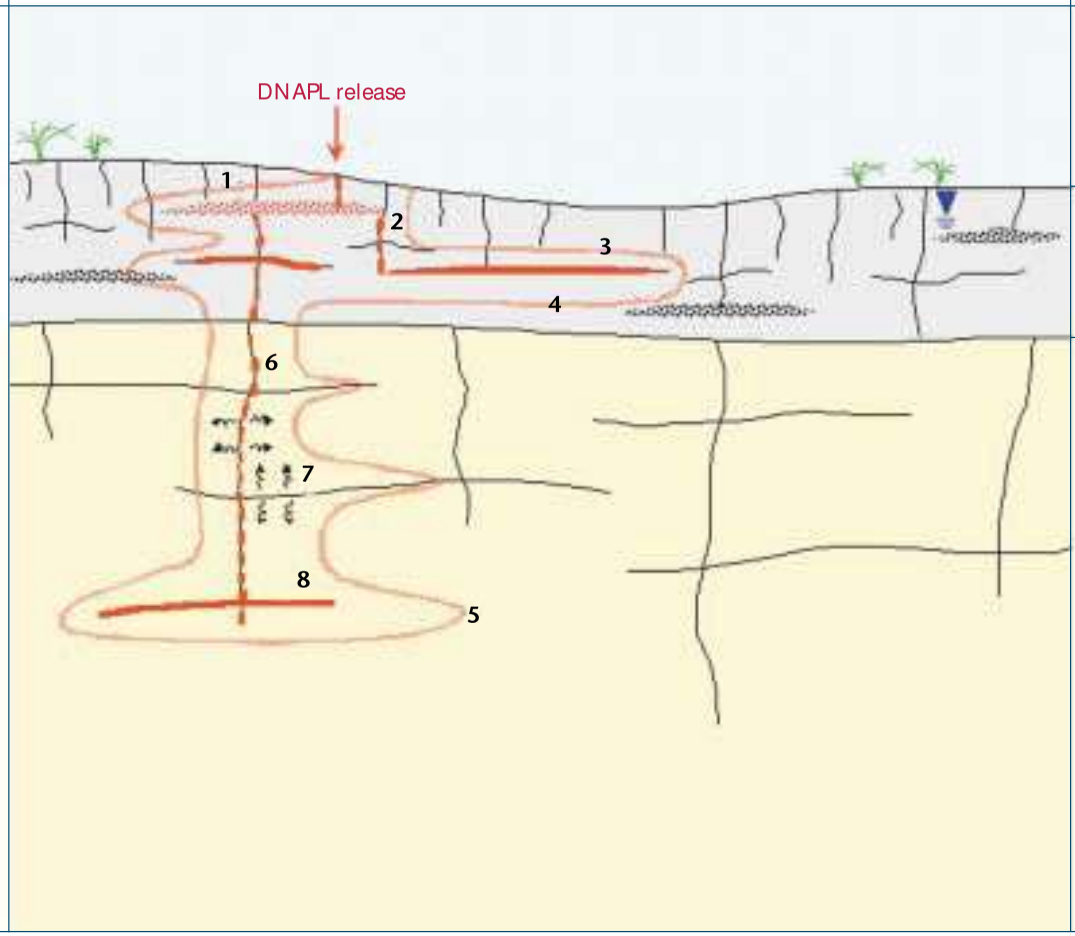
Features	DNAPL release into thin veneer of clay rich till	Domain
1 Residual DNAPL in sand lens 2 Residual DNAPL in fractures 3 DNAPL in sand lens 4 Diffusion halo 5 Aqueous phase plume 6 Residual DNAPL in bedrock fractures 7 Aqueous phase diffusion in bedrock matrix 8 Pooled DNAPL in bedrock fracture		Surface Drift fractured till (saturated) Bedrock (saturated)

Figure 22 DNAPL release into a thin veneer of clay-rich till

The porous nature of the till matrix allows migration of vapours in unsaturated regions of the till and for aqueous phase diffusion of contaminants in water-saturated regions.

Soil sampling conducted in the till may reveal low levels of contamination associated with the diffusion halos originating from the fractures and sand seams. The use of angled borings can increase the probability of encountering vertical fractures.

The degree of lateral DNAPL migration is greater for lower density DNAPLs such as creosote and coal tar, and less for higher density DNAPLs such as chlorinated solvents. With respect to plume migration, matrix diffusion into the clay matrix will significantly retard the rate of aqueous phase contaminant migration relative to the rate of groundwater flow. This means that the plume may not be far ahead of the DNAPL source zone, particularly for compounds that exhibit a high degree of sorption and moderate-to-high amounts of biodegradation.

8.7 DNAPL release into a sand/gravel aquifer

Figure 24 illustrates two DNAPL releases into a sand/gravel aquifer; the DNAPL on the left is creosote and the DNAPL on the right is a chlorinated solvent. For both releases, residual and pooled DNAPL are present in the unsaturated zone as well as below the water table. There is a general lack of vapour presence above the water table for the creosote release, but substantial vapour phase contamination for the chlorinated solvent. In addition, in this example, much of the chlorinated solvent DNAPL in the unsaturated zone has vapourised itself out of existence because of its volatile nature. Characterisation activities in the unsaturated zone include soil sampling for both releases, with the addition of vapour sampling for the solvent release. The chlorinated solvent vapours will have a much longer lifespan in the unsaturated zone than residual and pooled DNAPL.

The volume of release was sufficient in each case to reach a basal clay layer overlying bedrock. The solvent DNAPL encountered an erosional window in the clay layer and has entered the fractured bedrock below. The creosote DNAPL did not encounter any windows in the clay and, therefore, is restricted to the sand/gravel aquifer. A well-defined plume has evolved below the water table for both types of DNAPL. The solvent plume exhibits greater spatial extent in the down-gradient direction as a result of advection and dispersion processes, combined with the fact that the solvent of interest does not readily degrade or sorb to aquifer minerals.

Site characterisation activities below the water table include the use of conventional hollow-stem auguring techniques to obtain soil samples and install monitoring wells, as well as a variety of push-device probes designed to obtain grab samples.

The grab groundwater sample results are used to decide the sites of permanent monitoring wells. Drilling into bedrock is approached with caution and proceeds only in areas where it has been shown that the sand/gravel aquifer is void of residual and pooled DNAPL. This is facilitated by taking continuous soil cores in the sand/gravel aquifer at the location of each proposed drilling location in the bedrock.

8.8 DNAPL release into made ground

Figure 25 illustrates a DNAPL release into made ground containing a variety of subsurface structures. DNAPL has leaked from an underground storage tank and found its way into the gravel backfill of a building footing. Preferential migration of DNAPL takes place along the gravel because of its low capillary resistance.

Figure 25 DNAPL release into made ground and the effects of construction activities and services DNAPL also migrates to depth along abandoned piles, which also provide a pathway of low capillary resistance. The presence of residual and pooled DNAPL above the water table outside the building enclosure supports the potential for vapour diffusion and/or advection into the interior of the structure. Indoor air sampling is carried out to evaluate the presence and magnitude of vapour phase contamination.

Figure 25 also illustrates a second DNAPL release that has encountered the gravel backfill surrounding underground piping. The backfill provides a preferential pathway for DNAPL migration. DNAPL has also encountered an abandoned water supply well and has short-circuited to depth along the well. Site investigation techniques include conventional drilling and vapour sampling methods, but also include the use of geophysics to locate the buried structures.

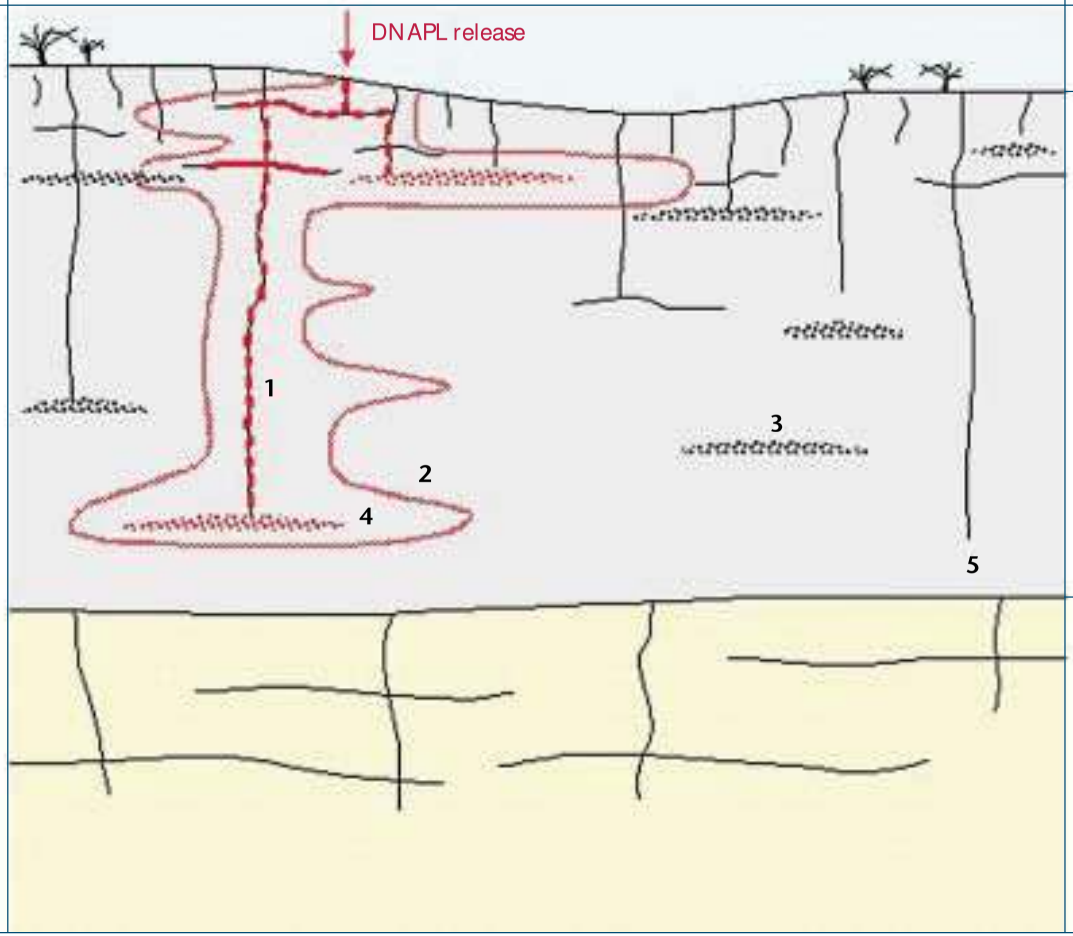
Features	DNAPL release into thick sequence of clay rich till	Domain
1 Residual DNAPL in fracture 2 Diffusion halo 3 Sand lens 4 DNAPL flow terminated in sand lens 5 No continuous fractures traversing the till		**Surface** **Drift fractured till** (saturated) **Bedrock** (saturated)

Figure 23 | DNAPL release into a thick sequence of clay till

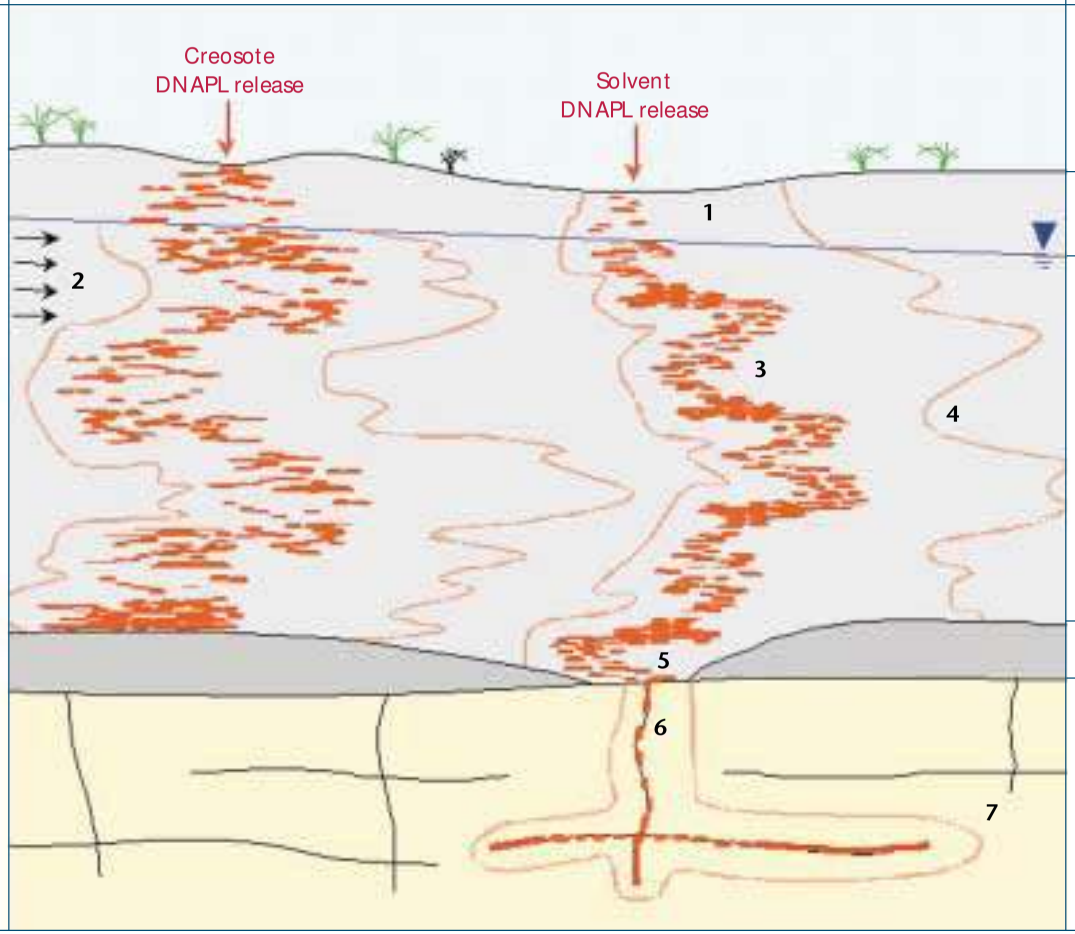
Features	DNAPL release into unconsolidated sand and gravel aquifer	Domain
1 Vapour plume 2 Groundwater flow direction 3 Residual and pooled DNAPL 4 Aqueous phase plume 5 Stratigraphic window (i.e. lateral discontinuity in unfractured clay horizon) 6 DNAPL entry into fractured rock 7 Matrix diffusion		Surface Drift (unsaturated) Drift (saturated) Unfractured Clay Fractured Bedrock (saturated)

Figure 24 DNAPL release into an unconsolidated sand/gravel aquifer

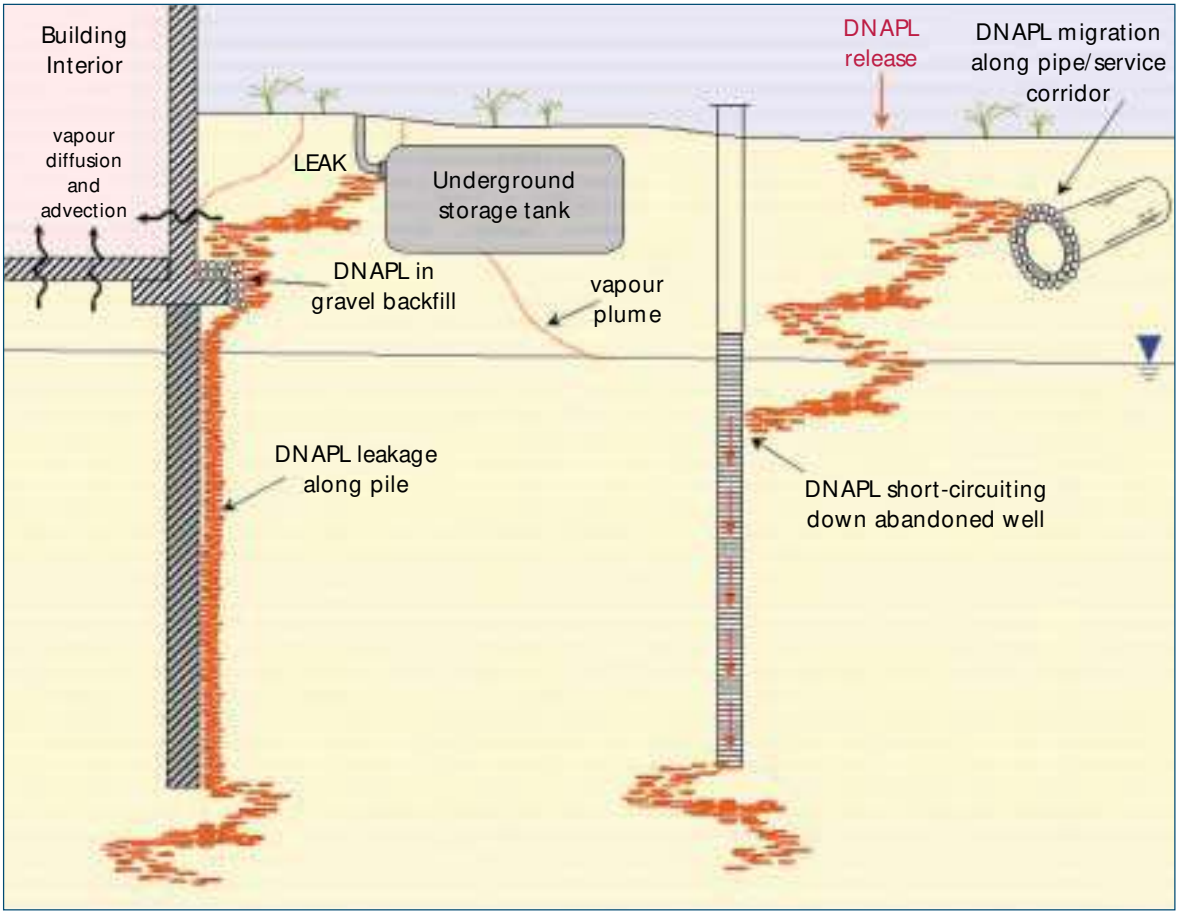


Figure 25 | DNAPL release into made ground and the effects of construction activities and services

Which parameters to measure at a site?

Objectives for site investigations are site-specific and depend on the potential source-pathway-receptor linkages (called 'pollutant linkages' under Part IIA of EPA 1990), the initial conceptual site model (and uncertainties therein), and the potential risks that need to be assessed and managed. The objectives of many site investigations may need to include: determining the presence of DNAPL; estimating the spatial extent of the DNAPL source zone; determining the presence of an aqueous phase plume; and, estimating the spatial extent of that plume, in order to allow a robust assessment of the risks that the pollution poses. Additional objectives may include estimating the rate of plume migration, assessing whether the plume is at steady-state, and assessing the degree of matrix diffusion that has occurred, along with a variety of other objectives that will form the basis for selecting a remediation strategy for the site.

Figure 26, in conjunction with the tables below, provide a brief summary of the parameters that can be measured at a site, along with a brief description of how the information can be used.

Table 9 lists a variety of contaminant characteristics that are useful in establishing a site conceptual model and in selecting a remediation strategy.

Other approaches

- employee interviews
- aerial photograph analysis
- outcrop mapping
- drilling
- down-hole logging
- laboratory analysis
- on-site analysis

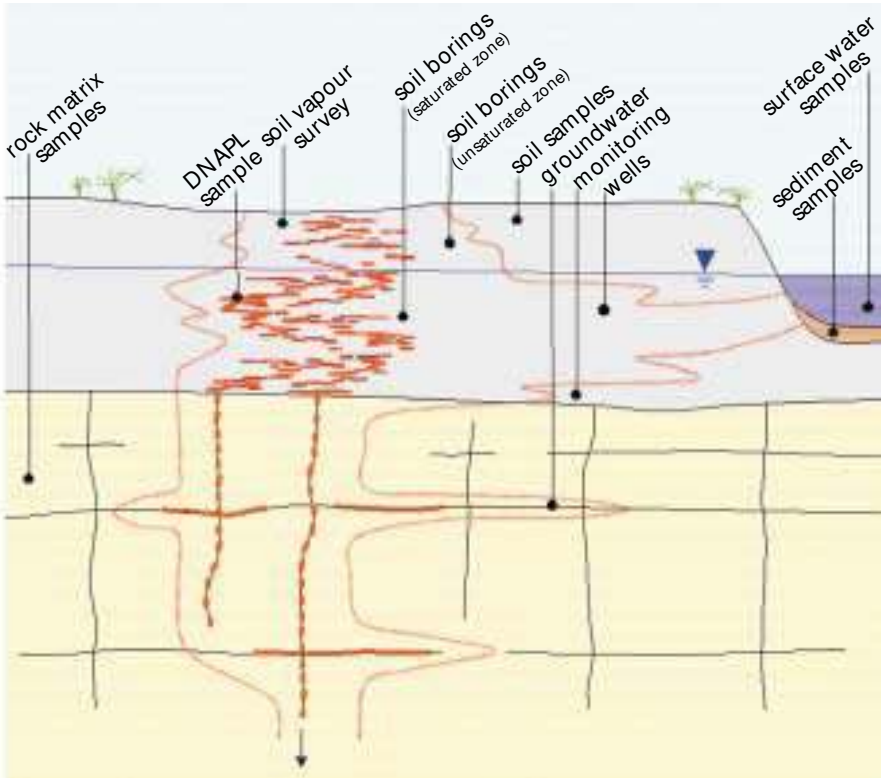


Figure 26 | Site investigation techniques

Table 9 | Contaminant characteristics to establish during site investigations

Parameter	Example use of information
DNAPL density	DNAPL mobility and pool height calculations
DNAPL viscosity	Determine if DNAPL could still be moving Design of NAPL recovery system
DNAPL component composition	Effective solubility calculations Predict future composition of plume
DNAPL-water interfacial tension	Determine importance of capillary forces Pool height calculations
Organic carbon partition coefficient	Determine degree of aqueous phase sorption and rate of plume migration
Contaminant half-life	Determine degree of degradation and rate of plume migration
DNAPL vapour pressure	Determine if vapour migration is a potential issue; Estimate lifespan of DNAPL above water table
Date and volume of DNAPL release	Estimate of depth of DNAPL migration. Is DNAPL still moving?
Potential DNAPL release locations	Help guide monitoring well placement

Measurement of the DNAPL properties requires the recovery of a sample of DNAPL from the subsurface. If this is not possible but the composition of the DNAPL is known, its density and viscosity can be estimated from literature sources.

DNAPL-water interfacial tension should not be estimated from handbooks, however, as this is a site-specific parameter which is influenced strongly by even small amounts of impurities. The organic carbon partition coefficient is typically obtained from literature sources, along with the DNAPL vapour pressure. The contaminant half-life depends on site-specific geochemical conditions and, therefore, should not generally be taken from handbooks or the literature; this parameter is typically determined through model calibration.

Information about the date and volume of DNAPL release is often not available, but efforts can be made to gain information from employees and by examining purchase records. Employee interviews, facility building plans and aerial photographs can be used to help determine the locations of potential DNAPL releases.

Table 10 | Unconsolidated deposit characteristics to determine during site investigations

Parameter	Example use of information
Porosity	Plume velocity calculation; Diffusion calculations
Dry bulk density	DNAPL threshold concentration calculation
Fraction organic carbon	Plume velocity calculation; DNAPL threshold calculation
Hydraulic conductivity	Plume velocity calculation; Design of extraction wells
Displacement pressure	Pool height calculations
Bulk retention capacity	DNAPL mass estimate
Contact angle	Refinement of conceptual model on DNAPL mobility
Hydraulic head distribution	Directions of groundwater flow and velocity of groundwater
Bedding structures	Directions of DNAPL migration
Spatial extent of DNAPL source zone	Guide remedy selection and design
Spatial extent of plume	Guide remedy selection; risk analysis

Table 10 lists a variety of parameters that may be needed at the various stages of site investigation, risk assessment and selection of remedial or management options and can be defined during the investigation of unconsolidated deposits such as sands, silts and gravels. The porosity, dry bulk density and fraction organic carbon are tests that can be conducted on samples of retrieved core.

Hydraulic conductivity is typically determined on a field-scale using pumping tests and slug tests. The displacement pressure of capillary barriers is usually not measured on a site-specific basis, but can be estimated from values of interfacial tension and hydraulic conductivity. The contact angle is usually assumed to be such that the system is water wet in the presence of DNAPL, but exceptions can occur. The hydrolic head distribution is typically determined through quarterly water level measurements in piezometers and monitoring wells. Bedding structures are determined from test pits, while the spatial extent of the DNAPL source zone and plume are determined using the techniques discussed in Section 7.

Table 11 lists a variety of parameters that can be determined as part of fractured rock and clay site investigations.

The matrix porosity, matrix dry bulk density and matrix fraction organic carbon need to be measured on samples obtained from a core. Each major rock type should be sampled as these parameters exhibit spatial variability. Although no specific number of samples can be dictated, a general rule of thumb is that 5-10 samples should be obtained during a site investigation.

The orientation of major fracture sets is typically determined through outcrop mapping and down-hole geophysical surveys. The fracture spacing is typically determined using the results of down-hole hydraulic testing in conjunction with core logs and an optical televiewer. It should be noted that core may contain mechanical breaks that can be difficult to distinguish from natural fractures.

The fracture porosity is typically determined from estimates of fracture spacing and estimates of fracture aperture determined from hydraulic testing. The bulk hydraulic conductivity is generally determined through pumping tests and slug tests, as well as hydraulic testing using straddle packer assemblies.

The bulk retention capacity of the rock mass for DNAPL is typically estimated from fracture porosity. The contact angle is usually assumed to provide a water-wet system, but site-specific measurements may be required if this assumption is questioned. The spatial extent of the DNAPL source zone and the aqueous phase plume are determined using the approaches discussed in Section 7.

Table 11 | Bedrock properties to determine during site investigations

Parameter	Example use of information
Matrix porosity **Matrix dry bulk density** **Matrix fraction organic carbon**	Diffusion calculations Estimate of remediation timeframe Estimate of (retarded) plume velocity
Orientation of major fracture sets	Determine direction of plume migration Directions of DNAPL migration
Fracture spacing	Diffusion calculations
Fracture porosity	Plume velocity calculation
Bulk rock hydraulic conductivity	Plume velocity calculation Design of extraction wells
Hydraulic head distribution	Directions of groundwater flow and velocity of groundwater
Bulk retention capacity	DNAPL mass estimate
Contact angle	DNAPL-rock-water wetting relationship
Spatial extent of DNAPL source zone	Guide remedy selection
Spatial extent of plume	Guide remedy selection; risk analysis

Basic Remediation Strategies

Remediation goals vary from site to site depending on regulatory jurisdiction, perceived and actual risks, site use, zoning issues, and the level of funding available. In the UK, remediation is typically undertaken to manage unacceptable risks to human health or the environment (Environment Agency, 1999). That is to say, remediation goals are risk-based. Remedial actions are usually selected taking account of the effectiveness, practicability, durability and likely costs and benefits of the various remediation options. The Environment Agency seeks to ensure that, within this framework, the most sustainable approach to remediation is selected. The area of contamination that is the focus of remediation may vary from site to site, but typically involves one or both of the following:

- DNAPL present within the source zone along with the associated aqueous and sorbed phase contamination in the source zone. If unsaturated media is involved, vapour phase contamination may also be addressed.
- Aqueous phase contamination present downstream of the DNAPL source zone. This will typically have sorbed phase contamination (on the soil or aquifer materials) associated with it and may include vapour phase contamination in unsaturated media.

These two categories distinguish between that region of the subsurface containing residual and pooled DNAPL (the source zone) and the associated aqueous phase plume present down-gradient of the source zone. This distinction is useful in that many remediation technologies are applicable only to one of these two zones. The most mobile form of contamination is often the aqueous phase plume originating from a stable configuration of residual and pooled DNAPL. If DNAPL is no longer moving at a particular site, only the aqueous phase plume migrating in groundwater and vapours in the unsaturated zone presents a means of spreading the extent of contamination.

10.1 Remediation goals within the DNAPL source zone

Remediation goals within the DNAPL source zone should aim to achieve risk-based objectives. They may include one or more of the following:

- Complete removal of all DNAPL, aqueous phase, sorbed phase and vapour phase contamination within the source zone. This remediation goal is typically referred to as **source zone restoration**.
- Removal of sufficient DNAPL mass from the source zone such that the length of the resulting aqueous phase plume downstream of the source zone will be subject to effective natural attenuation processes that stabilise and subsequently reduce the plume. This remediation goal is typically referred to as **partial mass removal**.
- Reduction of saturations within DNAPL pools to residual levels such that the DNAPL is stabilised. This remediation goal may be appropriate at sites where the DNAPL is still moving or where DNAPL pools may start moving as a result of drilling, excavation or pumping activities. This remediation goal is typically referred to as **stabilisation of mobile DNAPL**.
- Hydraulic or physical containment of the DNAPL source zone such that aqueous phase plumes can no longer expand. This remediation goal is typically referred to as **source zone containment**.

Source zone restoration has not yet been achieved at any sites where appreciable quantities of DNAPL are present below the water table. Source zone restoration is an extremely challenging goal that is likely to be attainable only at well-characterised sites exhibiting simple geology, shallow depths of contamination and simple contaminants such as single component NAPLs. Many of the UK geological settings of contamination (such as those that include fractured rock) are likely to mean that source zone restoration is (currently) infeasible, although incomplete source zone restoration may still bring about the achievement of risk-management objectives.

Partial mass removal is an attainable goal at some sites. However, great uncertainty remains regarding the amount of NAPL mass removal required to achieve a specified reduction in groundwater concentrations down-gradient of the source zone. Because the concentration exiting the source zone is a primary factor influencing the length of steady-state plume that will develop, there is uncertainty regarding the relationship between mass removal and the likelihood of achieving an effective natural attenuation remedy for the site. It has been established that there is not a linear relationship between mass removal and end-point groundwater concentrations. Removing 50 per cent of the NAPL mass, for example, does not lead to a 50 per cent reduction in groundwater concentrations. This stems from the fact that the concentration derived from residual and pooled NAPL is not related to the mass of NAPL present, but rather to many complicated factors such as NAPL-water contact area, the configuration of residual and pools, and groundwater velocity.

The relationship between mass removal and length of steady-state plume is illustrated in **Figure 27**. **Figure 27a** depicts a current situation where the aqueous phase plume extends beyond the compliance boundary. The compliance boundary may be set at a property boundary or an off-site receptor such as a river, lake or public supply well. **Figure 27b** illustrates a shorter steady-state plume that has been affected as a result of NAPL mass removal within the source zone. The steady-state plume no longer extends to the compliance boundary, implying that a sufficient amount of NAPL mass has been removed from the source zone.

While partial mass removal may not bring about a significant short-term reduction in groundwater contaminant concentrations, it is likely to reduce the duration over which the source and plume persist. This may be an important in achieving a sustainable solution that avoids bequeathing the burden of pollution to future generations.

Stabilisation of mobile NAPL has been achieved at a variety of sites and can be an appropriate remediation goal where NAPL is currently migrating or may start to migrate in the future. This remediation goal is typically considered at sites that have had very large releases of NAPL or at sites where the DNAPL has low mobility (for example, coal tar and creosote sites where the high viscosity and low density of the DNAPL leads to long timescales for migration). The reduction of saturations within NAPL pools can render them immobile, but will

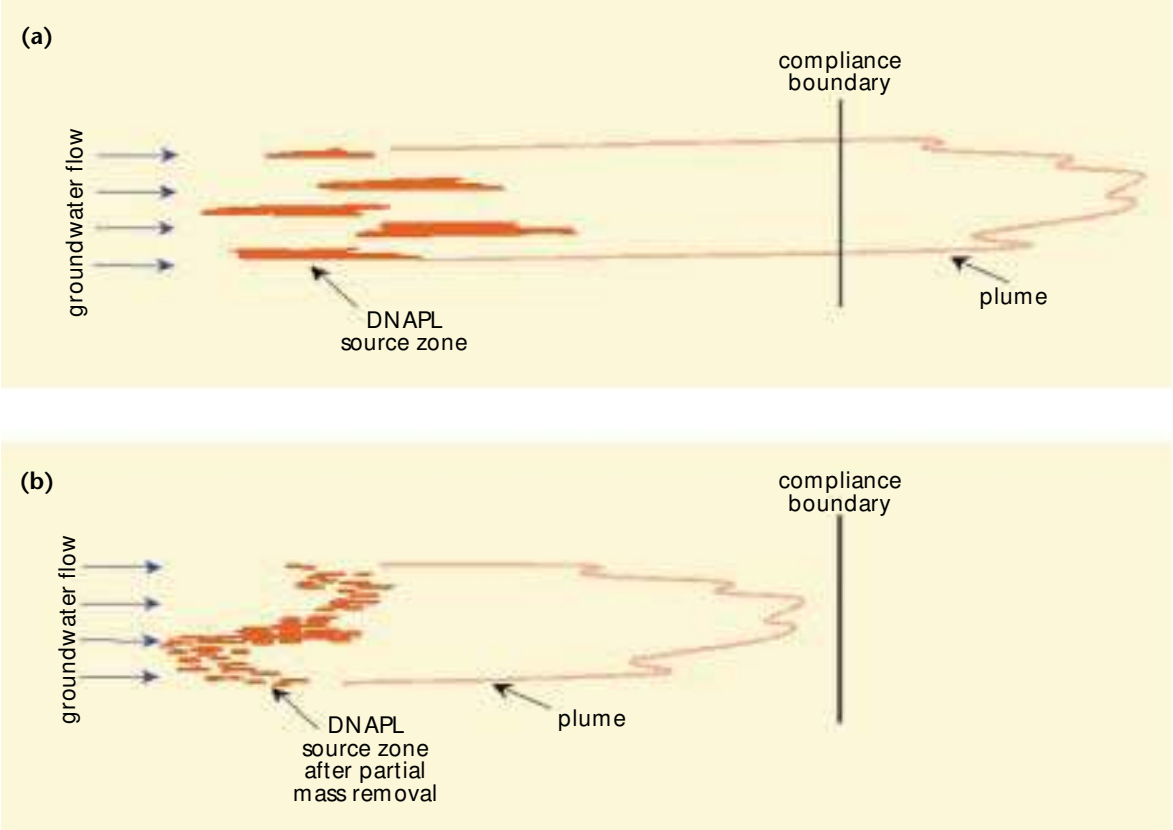


Figure 27 | (a) Steady-state plume prior to mass removal and (b) steady-state plume

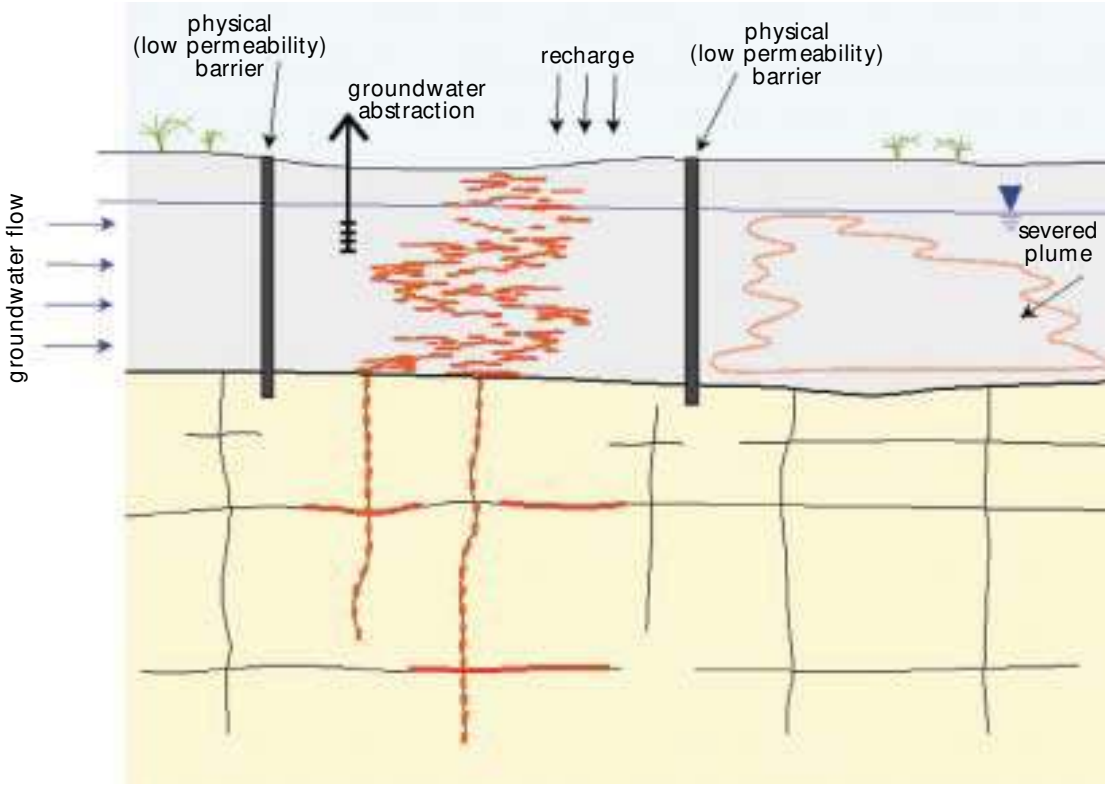


Figure 28 | Physical isolation of DNAPL source zone

generally not lead to a reduction of groundwater concentrations downstream of the source zone.

Source zone containment is often an achievable remediation goal that is implemented at sites where source zone restoration and partial mass removal are unlikely to be effective or will not achieve risk-management objectives. As illustrated in **Figure 28**, hydraulic or physical isolation of the NAPL source zone severs the down-gradient contaminant plume. Source zone containment typically requires long-term maintenance activities such as groundwater extraction from within physical barriers or continued operation and maintenance of a pump-and-treat system.

10.2 Remediation goals downstream of a DNAPL source zone

Remediation downstream of the DNAPL source zone should seek to manage risks to human health and the environment, and may include one or more of the following goals:

- Complete elimination of the groundwater plume, including removal of all aqueous and sorbed phase contamination. This remediation goal is typically referred to as **aquifer restoration**.
- Interception of the groundwater plume using either groundwater extraction wells or permeable reactive barriers (PRBs) such that contamination is eliminated down-gradient of the interception system. This approach is typically referred to as **plume interception**.
- Monitoring of groundwater concentrations and intrinsic processes to ensure that a steady-state (or ideally shrinking) plume has been achieved. This remediation approach is typically referred to as **monitored natural attenuation** and does not involve any physical human intervention (other than monitoring), but relies on naturally occurring processes to degrade and retard contaminants.

Aquifer restoration is rarely achieved at sites due to the long periods of time required to desorb contaminants from aquifer solids and the long periods of time associated with back-diffusion from the rock matrix and other low permeability features present in the subsurface. Aquifer restoration requires that the NAPL source zone be either completely removed or isolated from the groundwater flow system.

Plume interception is a commonly employed approach at sites where the presence of the groundwater plume is unacceptable. The design and construction of groundwater pump-and-treat systems, for example, is commonplace in many countries and has a considerable experience base (CIRIA, 1995).

Monitored natural attenuation recognises the fact that, after an initial period of expansion, all groundwater plumes will either reach a steady-state length or recede with time as a result of natural processes. Biological degradation is not a necessary requirement for natural attenuation, since dispersion alone will result in a steady-state plume. Because dispersion always occurs in the subsurface, all plumes will eventually reach a steady-state configuration. The superposition of biodegradation and dispersion, however, will lead to a shorter steady-state plume length (as illustrated in **Figure 29**). If degradation accelerates later, plumes can recede and become shorter. For sites where the source zone contains a multi-component NAPL, the progressive depletion of higher solubility, more mobile components can also lead to plume recession as the NAPL becomes enriched in lower solubility components.

Monitored natural attenuation typically requires good knowledge of the current extent of contamination, a good understanding of the groundwater flow system, an appropriate monitoring well network and several years of groundwater quality data to establish trends in concentration with time (Environment Agency, 2000).

10.3 Remediation technologies

The relatively recent awareness of soil and groundwater contamination by DNAPLs has resulted in the introduction of several innovative remediation technologies during the past ten years. While some technologies are relatively mature, others are still at the experimental stage and do not have a large experience base.

Some technologies target the DNAPL source zone only, while others can target both the source zone and the aqueous phase plume. This handbook is not intended to provide a detailed evaluation of remediation technologies. The aim of the following discussion, which provides a general overview of the various technologies currently available, is to help the reader decide which to examine further. Further discussion of DNAPL remediation technologies can be found in Environment Agency (2001b) and ITRC (2000).

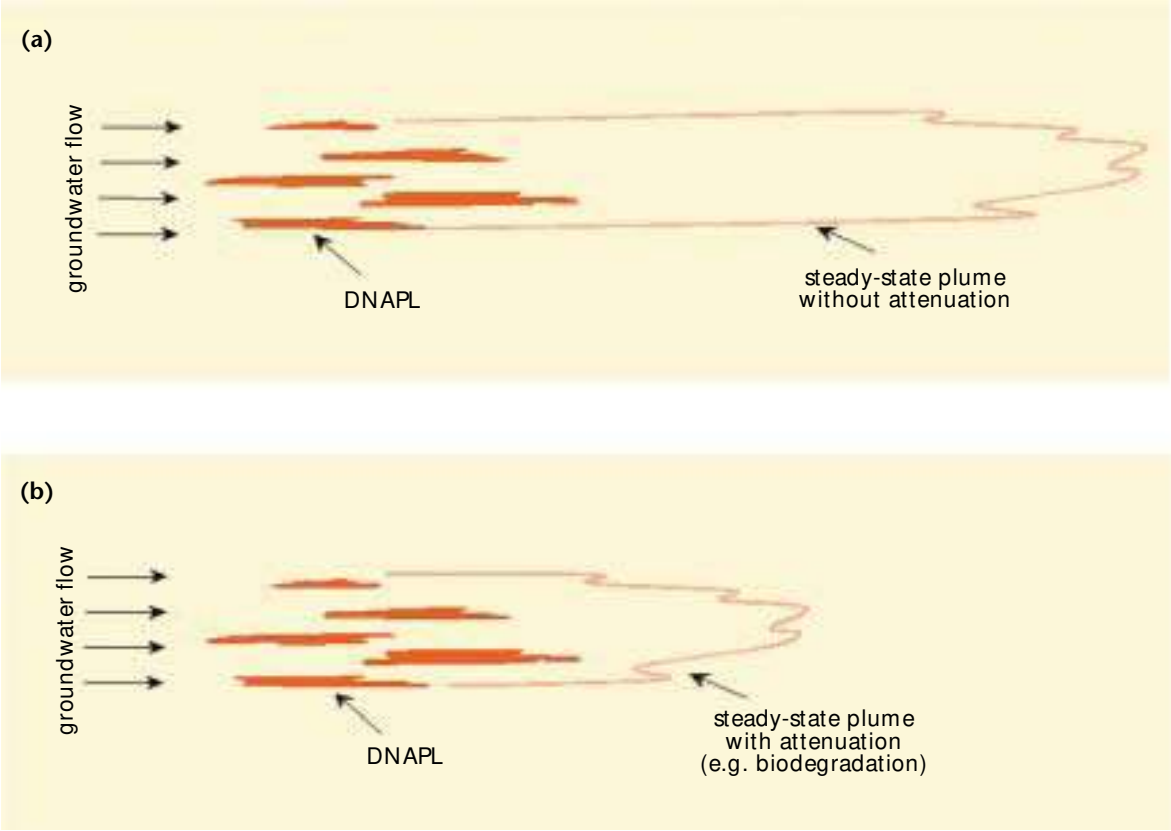


Figure 29 | Steady-state plumes (a) without and (b) with biodegradation

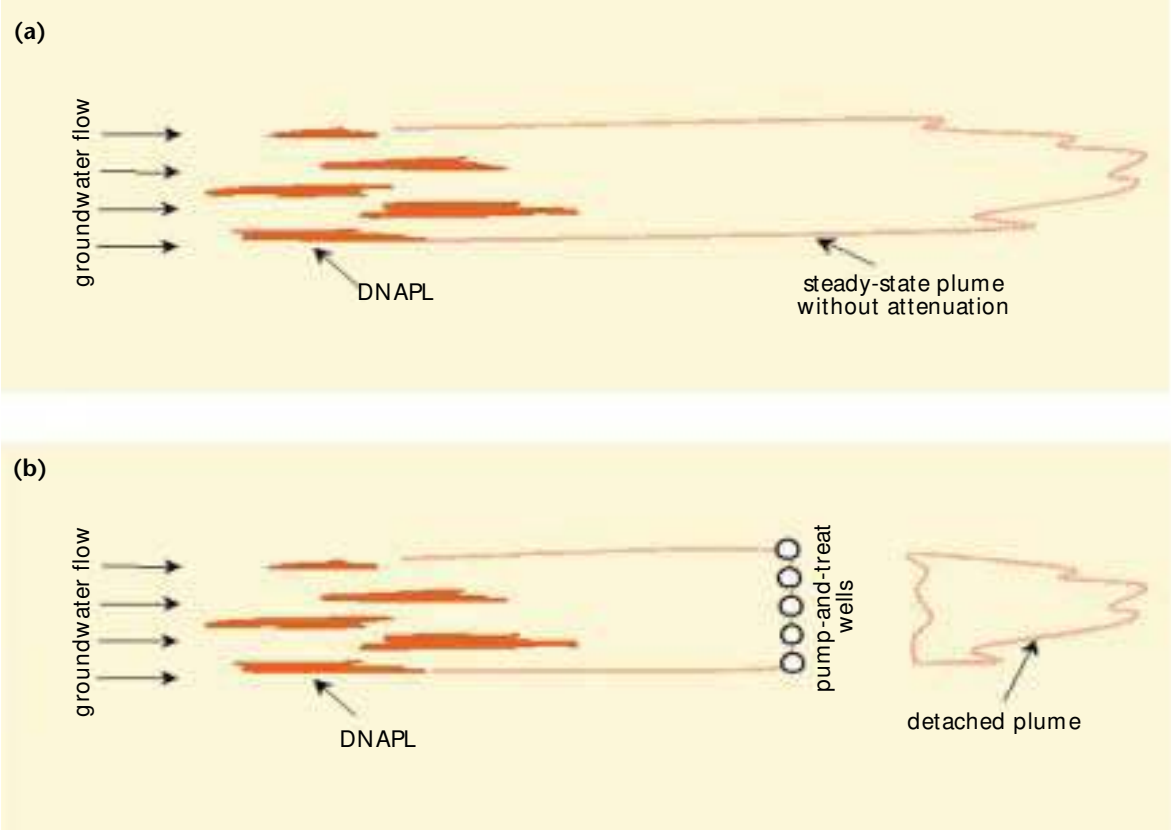


Figure 30 | Groundwater pump-and-treat

10.3.1 Groundwater pump-and-treat

The use of groundwater extraction wells to remove aqueous phase contamination and/or contain the DNAPL source zone hydraulically is a mature technology with a large base of experience (see for example CIRIA, 1998). The technology is generally suitable for all types of groundwater contaminants. Pumping groundwater creates a capture zone, within which all groundwater eventually flows into the extraction wells. This is depicted in **Figure 30**.

The extracted groundwater is typically treated ex situ in a treatment plant before being discharged to a watercourse, sewerage system or back to the ground. Because of the long time required to desorb contaminants from aquifer solids, the long timescales associated with back-diffusion from the rock matrix and the long time required to dissolve residual and pooled NAPL, most pump-and-treat systems operate for many decades.

10.3.2 Permeable reactive barriers

At sites where groundwater plumes are shallow and readily accessible, a trench or 'funnel and gate' type of PRB can be constructed and filled with suitable permeable reactive material(s). The groundwater plume flows naturally through the permeable barrier, within which degradation processes occur. If the residence time in the barrier is sufficient, groundwater concentrations exiting the downstream side of the barrier can achieve risk-based standards; otherwise, a PRB may be used in conjunction with monitored natural attenuation or an active remediation technique.

Permeable reactive barriers are a passive means of plume interception, which do not accelerate the removal of DNAPL from the source zone. Reactive iron is currently the most commonly employed barrier material. Reactive iron is only suitable for certain types of contaminants, however, and proper screening studies should be carried out before full-scale implementation (Environment Agency, 2002).

10.3.3 Physical barriers

Physical containment of the DNAPL source zone using sheet piling, injection grouting, secant piling and freeze walls is a means of physically isolating residual and pooled DNAPL from the groundwater flow system. A considerable base of experience exists within the geotechnical community with respect to the construction of such systems (see for example, CIRIA, 1996). Limited groundwater extraction is typically required from within the physical enclosure to offset infiltration and to ensure that leakage is inwards. The use of physical barriers is typically limited to unconsolidated deposits and requires good knowledge of the spatial extent of the DNAPL source zone.

10.3.4 Enhanced biodegradation

The injection of nutrients and other geochemical agents to stimulate biological activity is a means of degrading some contaminants in situ. If these agents are injected upstream of the DNAPL source zone, the accelerated degradation of contaminants in the aqueous phase will lead to an accelerated rate of DNAPL dissolution and can lower concentrations exiting the source zone.

Enhanced biodegradation is typically employed as a partial mass removal technology in order to achieve a shorter steady-state plume length down-gradient of the DNAPL source zone. There is a reasonably large base of experience associated with this technology, but its application is highly dependent on site-specific conditions (for example ambient geochemistry and contaminant composition) and proper screening tests and field pilot testing should be carried out before full-scale implementation.

10.3.5 Thermal technologies

Thermal technologies such as steam flooding, in situ thermal desorption (resistive heating), six-phase heating, radio frequency heating and microwave heating are relatively new technologies that rely on heat to vapourise and mobilise contaminants. Thermal technologies are applied within the DNAPL source zone and can be considered as a means of partial mass removal. They can be applied both above and below the water table, and require a soil vapour extraction system to contain and extract contaminant vapours.

Thermal technologies are still in the experimental stage, but several field trials and a limited number of full-scale applications have been completed. It is currently difficult to predict the amount of mass removal that can be achieved using thermal technologies at a particular site. The technologies are generally very aggressive and can carry a risk of mobilising contamination to previously un-impacted areas.

10.3.6 Chemical flushing to mobilise contaminants

Technologies such as surfactant flooding and alcohol flooding are relatively new technologies that can be used to mobilise and remove residual and pooled DNAPL within the source zone through either lowering interfacial tension or enhancing DNAPL solubility.

Chemical flooding is a means of partial mass removal that has been evaluated in several field trials with a wide range of results. It is currently difficult to predict the amount of mass removal that can be achieved using chemical flushing at a particular site. Chemical flushing is an aggressive means of mass removal, which can carry a risk of mobilising contaminants into previously un-impacted areas. In fractured rock, enhancing DNAPL solubility in fractures can lead to increased contaminant loading to the rock matrix.

10.3.7 Excavation

The physical removal of residual and pooled DNAPL from the source zone through excavation is often considered at sites where the extent of contamination is restricted primarily to unconsolidated deposits in the unsaturated zone. Factors to consider include the short-term risks of exposure, cost, accessibility and whether the completed excavation will result in risk reduction and an improvement in air or groundwater quality. If DNAPL is present below the water table, for example, the removal of contaminants from above the water table through excavation may not result in any improvement in groundwater quality, although it may reduce migration of vapours into the atmosphere or buildings.

10.3.8 Chemical flushing to destroy contaminants

Chemical agents such as oxidants can be used to destroy aqueous phase contaminants in situ. Oxidants are typically injected upstream of the DNAPL source zone such that the in situ destruction (oxidation) in the aqueous phase accelerates the rate of DNAPL dissolution.

Oxidant flooding is a relatively new technology that can be considered as a means of partial mass removal from the source zone. Several field trials and limited full-scale applications have been carried out with a wide range of results. When applied to fractured rock, oxidants have the potential to diffuse into the rock matrix and to destroy contaminants in situ. Common oxidants include Fenton's reagent, potassium/sodium permanganate and sodium persulphate. Because the oxidant demand of any naturally occurring organic carbon present in the subsurface can be high, screening studies and field pilot testing should be carried out before considering full-scale application (ITRC, 2001).

10.3.9 Soil vacuum extraction

Soil vacuum extraction (SVE) involves withdrawal of air from the unsaturated zone to:

- accelerate the vapourisation of residual and pooled DNAPL;
- the volatilisation of contaminants from soil moisture;
- the desorption of contaminants from aquifer solids.

SVE is a relatively mature technology that has seen widespread application at sites impacted by volatile organic compounds (VOCs). It is commonly used in combination with other techniques such as thermal technologies or air sparging. SVE (in isolation or in combination with other technologies) can meet soil-based remediation goals and tends to work best at sites characterised by low moisture contents and moderate to high permeability.

Although de-watering has been considered to extend the depth of application of SVE, this is generally not warranted because de-watered soils are likely to exhibit low air permeability. In addition, the removal of contamination from deep within the unsaturated zone is unlikely to lead to a significant improvement in groundwater quality if DNAPLs are present below the water table. De-watering also carries with it a risk of mobilising DNAPL pools deeper into the subsurface.

10.3.10 Water flooding

The mobilisation and removal of pooled DNAPL through increases in the hydraulic gradient is referred to as water flooding, and is a means of halting DNAPL migration and removing potentially mobile pools. The petroleum industry has considerable experience of water flooding and the technique has been applied at some hazardous waste sites where large volumes of DNAPL are present in the subsurface.

Water flooding is a source zone stabilisation technology that is relatively straightforward to implement. It does not remove residual DNAPL, however, implying that groundwater concentration reduction may not be associated with the mass removal activity.

10.3.11 Air sparging

Air sparging refers to the injection of air below the water table within the DNAPL source zone such that contaminants partition into the rising stream of air and thus accelerate DNAPL dissolution.

Air sparging is a partial mass removal technology that has not seen widespread success at DNAPL sites, although it has been used with greater success in combination with SVE at petrol spill sites. While some mass removal has been demonstrated, intimate contact between residual and pooled DNAPL and the rising air is difficult to achieve because of heterogeneity.

Glossary

Biodegradation
The degradation of contaminants in either the unsaturated or saturated zones as a result of biological activity. The rate of biodegradation depends on factors such as the presence of micro-organisms capable of degrading the contaminant(s), availability of electron acceptors, temperature and the specific contaminant of interest. Biodegradation typically results in the formation of daughter products, which may or may not biodegrade in the system of interest. Biodegradation manifests itself as lower contaminant (parent) concentrations in groundwater and a shorter steady-state plume. If oxygen is the primary electron acceptor, the degradation process is referred to as aerobic. Anaerobic degradation occurs when oxygen has been depleted and other electron acceptors such as nitrate, sulphate, iron or manganese facilitate degradation.

Capillary pressure
The pressure difference between the non-wetting fluid and the wetting fluid. Capillary pressure arises because of interfacial tension. The capillary pressure is directly proportional to the interfacial tension, and inversely proportional to the radius of curvature of the fluid-fluid interface. Usually expressed in Pascals (Pa).

Density
Mass per unit volume. Usually expressed in kg/m^3 for liquids such as DNAPLs.

Dispersion
The spreading of aqueous phase contaminants due to small-scale velocity variations in both porous and fractured media. Because of dispersion, concentrations decrease towards the leading and side edges of a plume.

DNAPL (dense non-aqueous phase liquid)
A liquid that is denser than water and only slightly soluble in water. DNAPLs exist in the subsurface as a separate fluid phase in the presence of either air or water, and can both vapourise into air and slowly dissolve into flowing groundwater. Examples include chlorinated solvents, creosote, coal tar and PCB oils.

DNAPL component composition
The composition of a DNAPL. The various components that combine to form the DNAPL phase are each present at a specific mass fraction. In some cases, the DNAPL of interest may be a single component liquid (for example, pure trichloroethene) and in other cases it may be composed of many different chemical constituents (for example, creosote).

DNAPL dissolution
The transfer of components present in the DNAPL to the water phase. Over time, the DNAPL composition will change as certain components dissolve out of the DNAPL earlier than other components. The effective solubility of these other components will therefore increase later.

Effective solubility
The aqueous solubility of a compound in (ground)water, where that compound is derived from a multi-component DNAPL. The effective solubility is proportional to the molar fraction of that compound in the DNAPL and the compound's single-component solubility (as described by Raoult's law).

Fracture entry pressure
The threshold capillary pressure required for a non-wetting fluid to enter a wetting-fluid saturated fracture. Fracture entry pressures are directly proportional to the interfacial tension and inversely proportional to the fracture aperture. Usually expressed in Pascals (Pa).

Fracture porosity
Volume of open fractures per unit volume of bulk rock. Typical values range between 0.001 and 0.01 (that is, 0.1-1 per cent).

Interfacial tension

A tensile force that exists in the interface between immiscible fluids. Without interfacial tension, DNAPLs would be fully miscible (infinitely soluble) in water. The fact that interfacial tension exists between a DNAPL and water is a defining feature of a DNAPL. Interfacial tension can be measured in the laboratory; typical units are N/m and dynes/cm (1,000 dynes/cm = 1 N/m). Interfacial tension exists between any pair of immiscible fluids such as air and water, DNAPL and water, and DNAPL and air.

LNAPL (light, non-aqueous phase liquid)

A liquid that is denser than water and only slightly soluble in water. LNAPLs exist in the subsurface as a separate fluid phase in the presence of either air or water, and can both vapourise into air and slowly dissolve into flowing groundwater. Examples include fuel oils such as diesel, petrol and heating oil.

Matrix diffusion

The transfer of contaminants dissolved in groundwater from open fractures to the rock or clay matrix. If concentrations are higher in the open fractures, diffusion will occur into the rock or clay matrix (forward diffusion). If concentrations are higher in the matrix, diffusion will occur out of the rock or clay matrix into water in the fractures (back-diffusion). As a consequence of matrix diffusion, contaminants in fractures will migrate more slowly than the groundwater.

Porous media displacement pressure

The threshold capillary pressure required for a non-wetting fluid to enter a wetting-fluid saturated porous medium. Lower permeability media such as silts and clays exhibit higher displacement pressures than more permeable media such as coarse sands and gravels. Usually expressed in Pascals (Pa).

Residual DNAPL

Disconnected blobs and ganglia of organic liquid (DNAPL) trapped by capillary forces in either porous or fractured media. Residual DNAPL forms at the trailing end of a migrating DNAPL body as a result of pore-scale hydrodynamic instabilities. Residual DNAPL saturations are typically between 5 per cent and 20 per cent of pore space for both porous media and fractures. Residual DNAPL is difficult to mobilise through increases in the hydraulic gradient (for example, aggressive groundwater pumping).

Plume

A contiguous region of groundwater containing dissolved contaminants. Plumes are typically formed by the dissolution of DNAPL into groundwater and therefore occur hydraulically down-gradient of the DNAPL source zone. Plume migration is subject to advection and dispersion, and may also be subject to sorption, biodegradation and matrix diffusion.

Pooled DNAPL

A continuous distribution of DNAPL in either porous media or fractures. DNAPL pools in porous media form above capillary barriers and typically range in both length and thickness from several centimetres to several metres. Pooled DNAPL is potentially mobile and is relatively easy to mobilise through increases in the hydraulic gradient (for example, as brought about by groundwater pumping). DNAPL pools in fractured media tend to form in horizontal and sub-horizontal fractures rather than vertical or steeply dipping fractures.

Sorption

The transfer of contaminants dissolved in water to the solid phase (typically fracture walls, the surfaces of sand/silt/clay grains or the surfaces of the solid portion of the rock matrix). Sorption is typically higher for more hydrophobic contaminants, and higher where greater amounts of naturally occurring organic carbon are present on the solid surfaces of interest.

Source zone

That region of the subsurface containing residual and/or pooled DNAPL.

Steady-state plume

The term applied to a contaminant plume that is no longer advancing in flowing groundwater. The time required to reach a steady-state configuration and the resulting length of the steady-state plume depend on factors such as groundwater velocity and the degree of dispersion, sorption and biodegradation occurring.

Vapourisation

The transfer of mass from the DNAPL phase to the air phase (often referred to as evaporation). The rate of vapourisation is proportional to the vapour pressure of the DNAPL, which in turn is temperature-dependent. Highly volatile DNAPLs such as some chlorinated solvents will vapourise quicker than low volatility DNAPLs such as PCB oils. In a multi-component DNAPL, the individual compounds with high vapour pressures will vapourise more quickly than those with lower vapour pressures, resulting in an enrichment of the DNAPL in the low vapour pressure compounds over time (referred to as weathering).

Viscosity

The shear resistance to flow of a fluid. Higher viscosity (thicker) fluids migrate more slowly in the subsurface than lower viscosity (thinner) fluids. Viscosity is temperature-dependent and should be measured in the laboratory at the subsurface temperature of interest. Typical units include Pascal seconds (Pa s), centipoises (cP), and centistokes (cSt).

Volatilisation

The transfer of contaminants dissolved in water to the air phase. Volatilisation is characterised by the Henry's law constant of the dissolved contaminant of interest.

Wettability

Describes the affinity of one fluid for a solid surface in the presence of a second fluid. The fluid that preferentially wets the solid surface is referred to as the wetting fluid and the other as the non-wetting fluid. A perfectly wetting fluid spreads spontaneously to coat the solid surface. A perfectly non-wetting fluid repels the solid surface and typically forms a spherical (beaded) shape on the solid surface. In many subsurface systems, water is wetting with respect to air, DNAPL is wetting with respect to air, and water is wetting with respect to DNAPL. Wettability is quantified by the contact angle, which is the angle measured between the fluid-fluid interface and the solid surface at the point of contact with the solid. Wettability is dependent on the chemical composition of the groundwater, the chemical composition of the DNAPL and the chemical composition of the solid surface of interest.

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Appendix A:

DNAPL pool height above capillary barrier

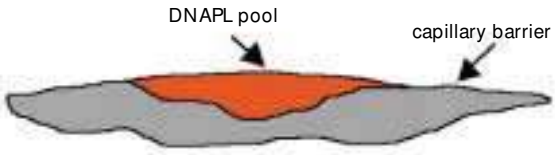

Figure A1 DNAPL pool above capillary barrier. The capillary barrier is assumed to be able to provide both vertical and lateral resistance to pool movement in a hydrostatic system.

The height of DNAPL that can accumulate above a capillary barrier below the water table can be estimated using Equation 8 (Kueper et al., 1993):

Equation 8

$$H = \frac{P_c'' - P_c'}{(P_D - P_W)g}$$

where:

H is the height of pooled DNAPL;

P_c'' is the capillary pressure at the base of the pool;

P_c' is the capillary pressure at the top of the pool;

P_D is the DNAPL density;

P_W is the groundwater density;

g is the acceleration due to gravity.

Equation 8 assumes that a hydrostatic system exists; for the pool height in a flowing groundwater system, see Longino and Kueper (1995). The maximum stable pool height is obtained by setting P_c'' equal to the displacement pressure of the capillary barrier. The capillary pressure at the top of the pool, P_c', will depend on how the pool was formed. A reasonable assumption is to set the capillary pressure at the top of the pool equal to the terminal pressure of the medium containing the pool.

Equation 8 also assumes that water is wetting with respect to DNAPL. The influence of a non-zero contact angle is incorporated into the choice of P_c'' and P_c'. Equation 8 represents a one-dimensional force balance and therefore assumes that the lateral sides of the pool are constrained by media with appropriate displacement pressures. Shorter equilibrium pool heights will arise in media that do not provide lateral capillary resistance of the pool. The calculations used to create **Figure 4** (see Section 3) are summarised in **Table A1**.

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Table A1 | Maximum DNAPL pool heights (P_W = 1,000 kg/m^3 and g = 9.806 m/s^2 for all calculations)

		Creosote/ coal tar	Chlorinated solvent	Mixed DNAPL 3c
Silt	P_D (kg/m^3)	1050	1460	1100
(K=1x10^{-6}m/s)	$P_c^{"}$ (Pa)	4750	6650	2375
	$P_c^{'}$ (Pa)	2375	3325	1188
	IFT (N/m)	0.020	0.028	0.010
	Pool height (m)	4.844	0.737	1.211
Fine sand	P_D (kg/m^3)	1050	1460	1100
(K=1x10^{-5}m/s)	$P_c^{"}$ (Pa)	2400	3360	1200
	$P_c^{'}$ (Pa)	1200	1680	600
	IFT (N/m)	0.020	0.028	0.010
	Pool height (m)	2.447	0.372	0.612
Medium sand	P_D (kg/m^3)	1050	1460	1100
(K=1x10^{-4}m/s)	$P_c^{"}$ (Pa)	800	1120	400
	$P_c^{'}$ (Pa)	400	560	200
	IFT (N/m)	0.020	0.028	0.010
	Pool height (m)	0.816	0.124	0.203
Course sand	P_D (kg/m^3)	1050	1460	1100
(K=1x10^{-3}m/s)	$P_c^{"}$ (Pa)	100	140	50
	$P_c^{'}$ (Pa)	50	70	25
	IFT (N/m)	0.020	0.028	0.010
	Pool height (m)	0.102	0.016	0.025

IFT = DNAPL-water interfacial tension

Appendix B:

Fracture aperture required to stop migration in bedrock

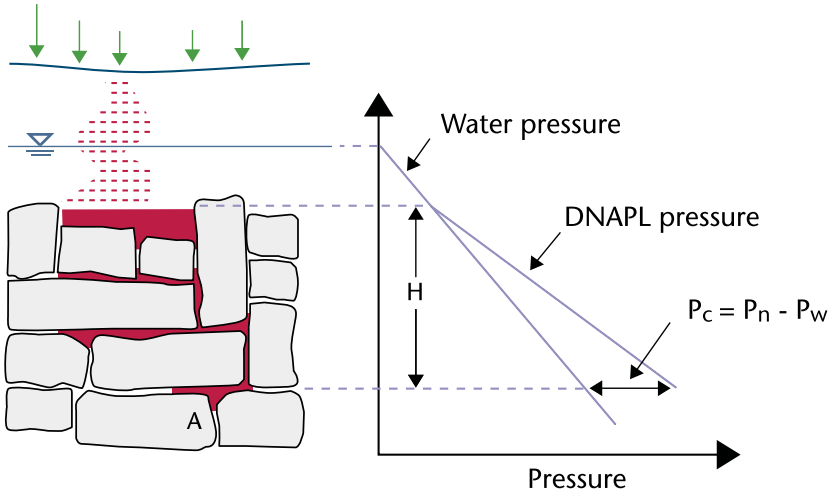

Figure B1 Vertical accumulation of DNAPL in a fracture network. Assuming a hydrostatic system, capillary pressure increases linearly with depth (modified after Kueper and McWhorter, 1991).

Consider the vertical accumulation of DNAPL in a fracture network depicted in **Figure B1**. It is assumed that there are no vertical components to groundwater flow and that the DNAPL has come to rest because of a narrowing of fracture apertures in the vicinity of point A. The narrowing of fracture aperture provides the capillary resistance to support the overlying distribution of DNAPL. The graph on the right hand side of **Figure B1** shows that both the groundwater and DNAPL pressures increase linearly with depth; thus, the capillary pressure also increases linearly with depth. The relationship between the vertical height of accumulated DNAPL (H) and the fracture aperture at A required to support the accumulation of DNAPL is given by:

Equation 9

$$H = \frac{2\sigma\cos\theta}{(P_N - P_W)ge}$$

where:

H is the vertical height of accumulated DNAPL;

σ is the DNAPL-water interfacial tension;

θ is the contact angle;

P_N is the DNAPL density;

P_W is the groundwater density;

g is the acceleration due to gravity;

e is the fracture aperture.

Equation 9 assumes that the top of the DNAPL accumulation exists at a capillary pressure of zero. In cases where the top of the accumulation is at a non-zero capillary pressure, a simple adjustment can be made to the equation. **Table B1** summarises the calculations used to produce **Figure 11** (see Section 5).

Table B1 Vertical accumulation of DNAPL in a fracture network. The fracture aperture (in µm) required to support accumulation of DNAPL is given (ρ_W = 1000 kg/m^3 and g = 9.806 m/s^2 for all calculations).

Height of accumulation (m)	Mixed composition DNAPL (µm)	Coal tar/creosote (µm)	TCE (µm)
0.1	407.9	815.8	88.7
0.2	203.9	407.9	44.3
0.5	81.6	163.2	17.7
1.0	40.8	81.6	8.9
2.0	20.4	40.8	4.4
3.0	13.6	27.2	2.9
4.0	10.2	20.4	2.2

IFT = DNAPL-water interfacial tension. All three DNAPLs are assigned IFT = 0.020 N/m.
DNAPL densities are: 1,100 kg/m^3 (mixed composition); 1,050 kg/m^3 (coal tar/creosote) and 1,460 kg/m^3 (TCE).

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Appendix C:

Soil concentration calculation in the absence of DNAPL composition analysis

For a multi-component DNAPL of unknown composition, the sum of the mole fractions must equal one. DNAPL will therefore be present in a soil sample if the following condition is met:

Equation 10

$$\sum_{i=1}^{n} \frac{C_{obs}^{T}}{C_{S}^{T}} \leq 1$$

where:

C_{obs}^{T} is the reported concentration of component i;

C_{S}^{T} is the single component soil concentration of component i;

n is the total number of components observed in the soil sample.

As an example, consider a soil sample that has been shown by the laboratory to contain trichloroethene at a concentration of 145 mg/kg, tetrachloroethene at a concentration of 155 mg/kg, tetrachloromethane at a concentration of 200 mg/kg, chlorobenzene at a concentration of 177 mg/kg and 1,1,1-trichloroethane at a concentration of 213 mg/kg. **Table C1** illustrates implementation of Equation 10 to determine whether these concentrations correspond to the presence of a multi-component DNAPL in the soil sample. The soil sample has been collected from below the water table in a sand aquifer characterised by a porosity of 25 per cent, a fraction organic carbon of 0.003 and a dry bulk density of 1,990 kg/m^3. The last column of **Table C1** sums to greater than 1.0, indicating that DNAPL was present in the soil sample.

Table C1 | Soil concentration calculation for multi-component DNAPL

Compound	C_{obs}^{T} (mg/kg)	K_{oc} (l/kg)	Solubility (mg/l)	C_{S}^{T} (mg/kg)	$\frac{C_{obs}^{T}}{C_{S}^{T}}$
trichloroethene	145	126	1,100	554	0.262
tetrachloroethene	155	364	200	244	0.636
tetrachloromethane	200	439	790	1,140	0.175
chlorobenzene	177	330	500	558	0.317
1,1,1-trichloroethane	213	152	1320	768	0.277
				SUM =	**1.668**

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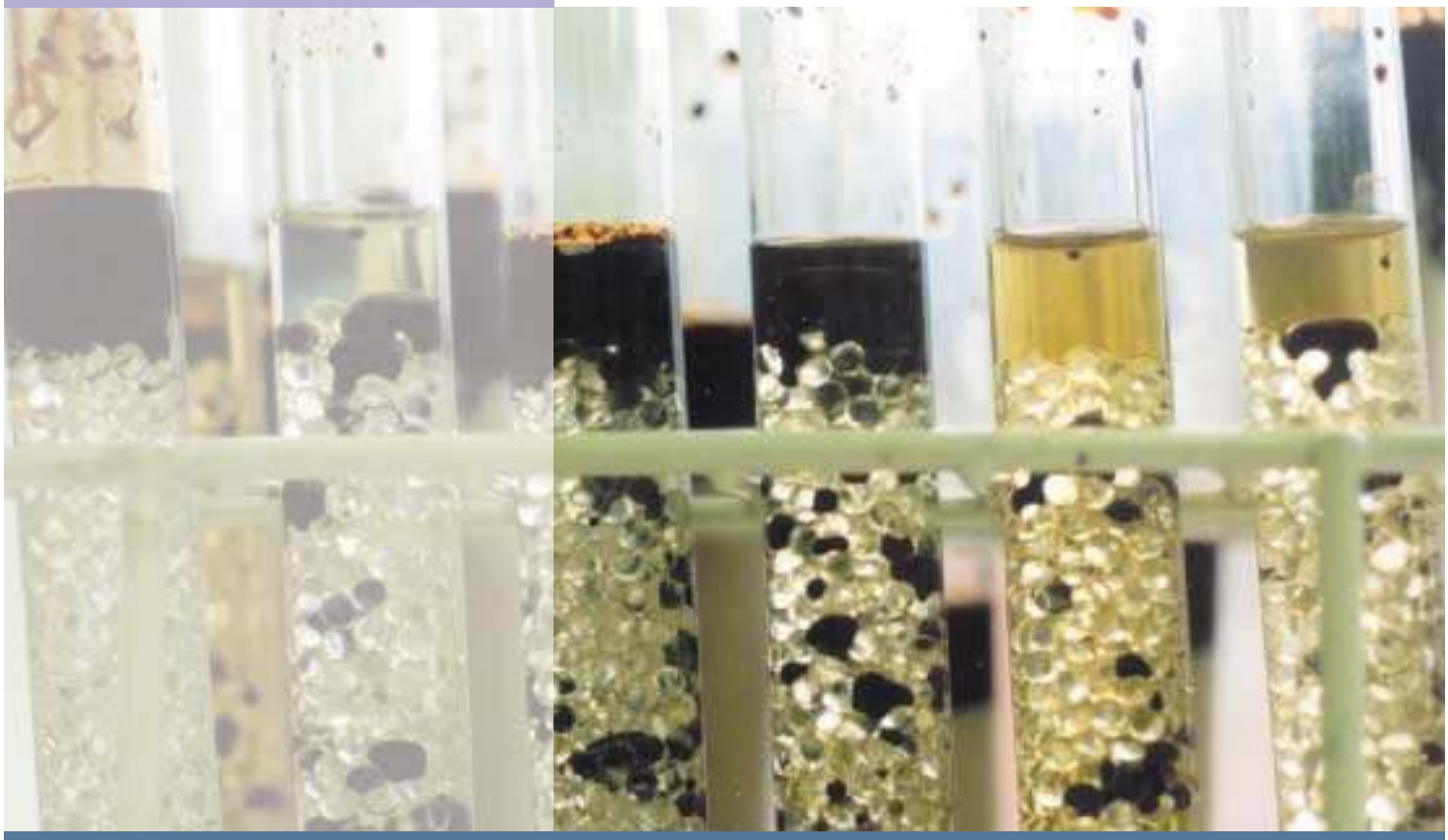

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